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## Three concomitant C–C dissociation pathways during the mechanical activation of an N-heterocyclic carbene precursor

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## 2 General Experimental Details

Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

Gel permeation chromatography (GPC) analyses were performed in THF solution (1 mg mL<sup>-1</sup>) at 35 °C using a Malvern Viscotek GPCmax VE2001 solvent/sample module with 2 × PL gel 10 µm mixed-B and a PL gel 500 Å column, and equipped with a Viscotek VE 3240 UV/vis multichannel detector and Viscotek VE3580 refractive index detector employing narrow polydispersity polystyrene standards (Agilent Technologies) as a calibration reference. Samples were filtered through a Whatman Puradisc 4 mm syringe filter with 0.45 µm PTFE membrane before injection to equipment, and experiments were carried out with injection volume of 100 µL, flow rate of 1 mL min<sup>-1</sup>. Results were analysed using *n*-dodecane as an internal marker using Malvern OmniSEC 5.10 software.

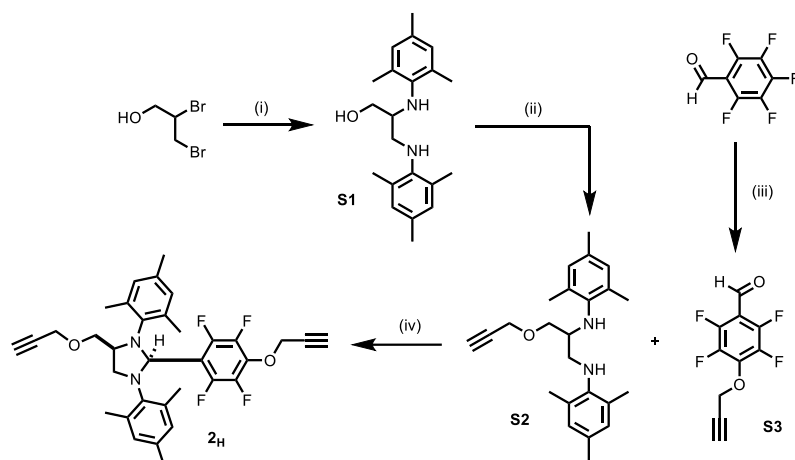
Ultrasound experiments were performed using a Sonics VCX 500 ultrasonic processor equipped with a 13 mm diameter solid probe or replaceable-tip probe. The distance between the titanium tip and the bottom of the Suslick cell was 3 cm. The ultrasonic intensity was calibrated using the method outlined by Hickenboth *et al.*<sup>1</sup>. The Suslick cells were fabricated by the School of Chemistry glass workshop at the University of Manchester.

Analytical TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F254, Merck, Germany) and observed under UV light or stained with either potassium permanganate or phosphomolybdic acid solution. Preparative TLC was performed on precoated silica gel plates: 2 mm, UNIPLATE GF, Analtech Inc., DE, USA. Flash column chromatography was performed with silica gel 60 (230-400 mesh) from Sigma-Aldrich. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using either a Bruker Avance III 500 MHz Prodigy instrument or a Bruker Avance III 400 MHz Prodigy instrument at the University of Manchester. Chemical shifts are reported in parts per million (ppm) from high to low frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in Hertz (Hz) and splitting patterns are designated as follows: br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Mass spectra were obtained through the Mass Spectrometry services in the School of Chemistry at the University of Manchester.

**Abbreviations:** APCI: atmospheric pressure chemical ionisation; DCM: dichloromethane; ESI: electrospray ionization; PE: petroleum ether; EtOAc: ethyl acetate; HRMS: high resolution mass spectrometry; MeOH: methanol; MS: mass spectrometry; THF: tetrahydrofuran; TLC: thin layer chromatography.

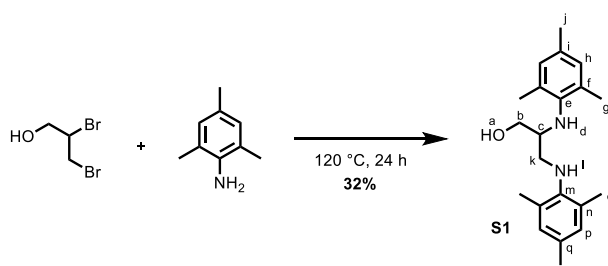
### 3 Synthesis of mechanophores and reference compounds

#### 3.1 Synthetic Route to **2<sub>H</sub>**



**Figure 1.** Synthetic route to **2<sub>H</sub>**. Conditions: (i) 2,4,6-trimethylaniline, 120 °C, 24 h, 32% yield; (ii) propargyl bromide, NaH, THF, 40 °C, 16 h, 90% yield; (iii) KO<sup>t</sup>Bu, propargyl alcohol, r.t., 5 min, 54% yield; (iv) acetic acid, r.t., 30 min, 69% yield.

##### 3.1.1 Synthesis of **S1**



2,3-dibromopropan-1-ol (2.36 mL, 23.0 mmol, 1.0 eq.) and 2,4,6-trimethylaniline (8.36 mL, 59.5 mmol, 2.6 eq.) were added together and heated to 120 °C for 20 h. After cooling to room temperature, aqueous NaOH solution (1.7 M, 200 mL) was added. The mixture was extracted with DCM (200 mL) and the organic layer dried over magnesium sulphate before being condensed to give the crude product as a dark brown liquid. Purification was carried out via column chromatography (SiO<sub>2</sub>, PE/EtOAc : 3/1) to give the product as a dark brown solid (2.40 g, 7.36 mmol, 32% yield).

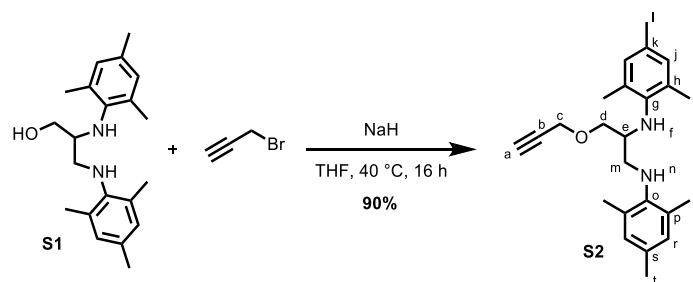
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 6.83 (s, 2H, H<sub>h</sub>), 6.81 (s, 2H, H<sub>p</sub>), 3.97 (dd, *J* = 11.0, 2.7 Hz, 1H, H<sub>b</sub>), 3.85 (ddd, *J* = 11.0, 4.2, 1.2 Hz, 1H, H<sub>b</sub>), 3.42 – 3.37 (m, 1H, H<sub>c</sub>), 3.23 (ddd, *J* = 12.0, 5.1, 1.2 Hz, 1H, H<sub>k</sub>), 3.00 (dd, *J* = 11.9, 3.9 Hz, 1H, H<sub>k</sub>), 2.30 (s, 6H, H<sub>g</sub>), 2.24 (s, 3H, H<sub>j</sub>), 2.23 (s, 3H, H<sub>r</sub>), 2.18 (s, 6H, H<sub>o</sub>).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ = 142.61 (C<sub>m</sub>), 141.94 (C<sub>e</sub>), 132.66 (C<sub>q</sub>), 131.05 (C<sub>i</sub>), 130.73 (C<sub>n</sub>), 129.93 (C<sub>h</sub>), 129.69 (C<sub>p</sub>), 128.90 (C<sub>f</sub>), 66.25 (C<sub>b</sub>), 57.02 (C<sub>c</sub>), 52.46 (C<sub>k</sub>), 20.71 (C<sub>j</sub>), 20.61 (C<sub>r</sub>), 19.07 (C<sub>g</sub>), 17.93 (C<sub>o</sub>).

**MS-ESI(+):** *m/z* = 327.3 (100, [M+H]<sup>+</sup>), 263.1 (90, [M-C<sub>9</sub>H<sub>12</sub>N]<sup>+</sup>).

**MS-ESI(-):** *m/z* = 325.3 (100, [M-H]<sup>-</sup>), 134.0 (15, [M-C<sub>12</sub>H<sub>18</sub>NO]<sup>-</sup>).

### 3.1.2 Synthesis of S2



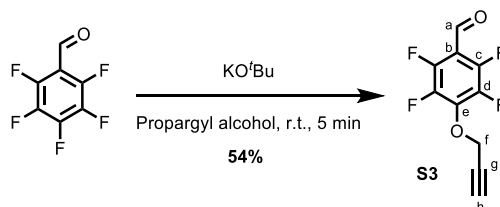
**S1** (2.40 g, 7.35 mmol, 1 eq.) and propargyl bromide (80% in toluene, 1.64 mL, 14.7 mmol, 2 eq.) were dissolved in dry THF (34 mL). Sodium hydride (60% in mineral oil, 0.88 g, 22.1 mmol, 3 eq.) was added slowly and the mixture stirred at 40 °C for 16 h. After cooling to room temperature, water (10 mL) was added and the mixture condensed to remove THF. The remaining aqueous mixture was extracted with DCM (3 x 20 mL). The combined organic layers were dried over sodium sulphate and condensed to give the crude product as a dark brown solid. Purification was carried out via column chromatography (SiO<sub>2</sub>, PE/EtOAc : 15/1) to give the product as a yellow/brown solid (2.40 g, 6.58 mmol, 90% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.85 (s, 4H, H<sub>j</sub>, H<sub>r</sub>), 4.16 (qd,  $J$  = 15.8, 2.4 Hz, 2H, H<sub>c</sub>), 3.82 – 3.39 (m, 5H, H<sub>d</sub>, H<sub>e</sub>, H<sub>f</sub>, H<sub>n</sub>), 3.31 (dd,  $J$  = 12.0, 5.9 Hz, 1H, H<sub>m</sub>), 3.06 (dd,  $J$  = 12.0, 5.9 Hz, 1H, H<sub>m</sub>), 2.44 (t,  $J$  = 2.4 Hz, 1H, H<sub>a</sub>), 2.31 (s, 6H, H<sub>i</sub>), 2.30 (s, 6H, H<sub>q</sub>), 2.27 (s, 6H, H<sub>l</sub>, H<sub>t</sub>).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 143.71 (C<sub>o</sub>), 141.67 (C<sub>g</sub>), 131.35 (C<sub>k</sub> or C<sub>s</sub>), 130.92 (C<sub>k</sub> or C<sub>s</sub>), 130.01 (C<sub>h</sub> or C<sub>p</sub>), 129.71 (C<sub>j</sub> or C<sub>r</sub>), 129.51 (C<sub>j</sub> or C<sub>r</sub>), 129.37 (C<sub>h</sub> or C<sub>p</sub>), 79.54 (C<sub>b</sub>), 74.84 (C<sub>a</sub>), 70.40 (C<sub>d</sub>), 58.56 (C<sub>c</sub>), 56.58 (C<sub>e</sub>), 50.64 (C<sub>m</sub>), 20.68 (C<sub>i</sub> or C<sub>t</sub>), 20.64 (C<sub>i</sub> or C<sub>t</sub>), 18.92 (C<sub>i</sub>), 18.44 (C<sub>q</sub>).

**MS-ESI(+)**:  $m/z$  = 365.4 (100, [M+H]<sup>+</sup>), 230.2 (80, [M-C<sub>9</sub>H<sub>12</sub>N]<sup>+</sup>), 387.3 (25, [M+Na]<sup>+</sup>).

### 3.1.3 Synthesis of S3



2,3,4,5,6-pentafluorobenzaldehyde (1.25 g, 6.38 mmol, 1 eq.) was dissolved in propargyl alcohol (10 mL). Potassium *tert*-butoxide (0.79 g, 7.01 mmol, 1.1 eq.) was separately dissolved in propargyl alcohol (10 mL) after which the mixture was added dropwise to the 2,3,4,5,6-pentafluorobenzaldehyde solution. The reaction mixture was stirred for 5 min before being condensed to remove propargyl alcohol. DCM (30 mL) and water (30 mL) were added to the resulting solid. The organic phase was separated and dried over sodium sulphate before being condensed to give the crude product as a yellow liquid. Purification was carried out via column chromatography (SiO<sub>2</sub>, PE/EtOAc : 50/1) to give the product as a colourless liquid (0.80 g, 3.45 mmol, 54% yield).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 10.23 (s, 1H, H<sub>a</sub>), 5.02 (m, 2H, H<sub>f</sub>), 2.61 (t,  $J$  = 2.4 Hz, 1H, H<sub>h</sub>).

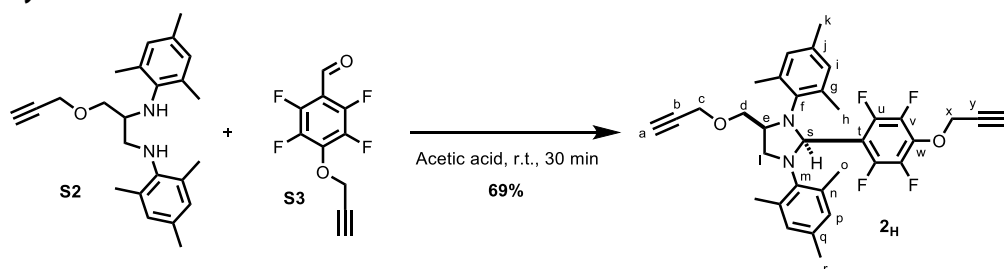
**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 182.27 – 182.10 (m, C<sub>a</sub>), 147.59 (dddd, *J* = 261.7, 12.7, 6.9, 3.9 Hz, C<sub>c</sub>), 142.18 – 139.83 (m, C<sub>d</sub>), 140.95 (tt, *J* = 11.6, 4.2 Hz, C<sub>e</sub>), 110.18 (t, *J* = 9.8 Hz, C<sub>b</sub>), 78.18 (C<sub>g</sub>), 76.38 (C<sub>h</sub>), 61.77 (t, *J* = 4.6 Hz, C<sub>f</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -145.88 – -145.98 (m, 2F, F<sub>c</sub>), -155.39 – -155.53 (m, 2F, F<sub>d</sub>).

**MS-ESI(+)**: *m/z* = 203.0 (100, [M-CHO]<sup>+</sup>), 239.1 (50, [M-C<sub>3</sub>H<sub>3</sub>+2Na]<sup>+</sup>).

**MS-APCI(-)**: *m/z* = 193.1 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

### 3.1.4 Synthesis of 2<sub>H</sub>



**S2** (100 mg, 0.27 mmol, 1 eq.) was dissolved in minimum acetic acid (approx. 0.3 mL). The solution was added to **S3** (64 mg, 0.27 mmol, 1 eq.) and the mixture stirred for 30 min. The resulting brown precipitate was filtered off and washed thoroughly with ice-cold methanol to give the pure product as a white solid (110 mg, 0.19 mmol, 69% yield).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 6.90 (s, 1H, H<sub>i</sub>), 6.76 (s, 2H, H<sub>p</sub>), 6.74 (s, 1H, H<sub>i</sub>), 6.33 (s, 1H, H<sub>s</sub>), 4.77 (s, 2H, H<sub>x</sub>), 4.16 (s, 2H, H<sub>c</sub>), 4.02 (t, *J* = 8.8 Hz, 1H, H<sub>d</sub>), 3.92 (t, *J* = 8.1 Hz, 1H, H<sub>i</sub>), 3.87 – 3.81 (m, 1H, H<sub>e</sub>), 3.69 (m, 2H, H<sub>i</sub>, H<sub>d</sub>), 2.54 (s, 3H, H<sub>h</sub>), 2.51 – 2.30 (br, 6H, H<sub>o</sub>), 2.47 (s, 1H, H<sub>z</sub>), 2.42 (s, 1H, H<sub>a</sub>), 2.23 (s, 3H, H<sub>k</sub>), 2.19 (s, 3H, H<sub>r</sub>), 2.00 (s, 3H, H<sub>h</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 147.91 – 144.77 (m, C<sub>u</sub>), 143.00 – 139.35 (m, C<sub>v</sub>), 140.43 (C<sub>g</sub>), 140.06 (C<sub>f</sub>), 139.39 – 138.86 (br, C<sub>n</sub>), 137.61 (C<sub>m</sub>), 137.30 – 136.69 (br, C<sub>n</sub>), 136.96 (C<sub>g</sub>), 136.38 (C<sub>j</sub>), 135.44 (C<sub>q</sub>), 134.96 (t, *J* = 12.4 Hz, C<sub>w</sub>), 131.11 (C<sub>i</sub>), 130.73 – 130.33 (br, C<sub>p</sub>), 130.15 – 129.74 (br, C<sub>p</sub>), 129.51 (C<sub>i</sub>), 115.22 (t, *J* = 11.0 Hz, C<sub>t</sub>), 79.95 (C<sub>b</sub>), 77.21 (C<sub>z</sub>), 77.06 (C<sub>y</sub>), 74.54 (C<sub>a</sub>), 73.68 (C<sub>s</sub>), 73.10 (C<sub>d</sub>), 62.60 (C<sub>e</sub>), 61.52 (t, *J* = 3.9 Hz, C<sub>x</sub>), 58.58 (C<sub>c</sub>), 53.93 (C<sub>i</sub>), 20.88 (C<sub>k</sub>), 20.75 (C<sub>r</sub>), 20.24 (C<sub>h</sub>), 20.50 – 20.03 (br, C<sub>o</sub>), 18.76 – 18.35 (br, C<sub>o</sub>), 18.31 (C<sub>h</sub>), 18.29 (C<sub>h</sub>).

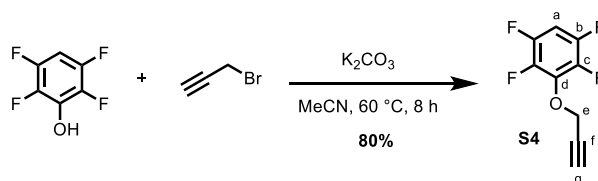
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -137.30 (dd, *J* = 20.8, 9.4 Hz, 1F, F<sub>u</sub>), -148.19 (dd, *J* = 22.4, 8.7 Hz, 1F, F<sub>u</sub>), -156.98 (dd, *J* = 20.9, 8.7 Hz, 1F, F<sub>v</sub>), -157.11 (dd, *J* = 22.2, 9.4 Hz, 1F, F<sub>v</sub>).

**MS-ESI(+)**: *m/z* = 365.2 (100, [M-C<sub>10</sub>H<sub>4</sub>F<sub>4</sub>O+3H]<sup>+</sup>), 375.3 (80, [M-C<sub>9</sub>H<sub>3</sub>F<sub>4</sub>O]<sup>+</sup>), 579.2 (20, [M+H]<sup>+</sup>).

**MS-ESI(-)**: *m/z* = 539.3 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

**HRMS-ESI(+)**: 579.2636 [M+H]<sup>+</sup>, calculated for C<sub>34</sub>H<sub>35</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>: 579.2629.

### 3.2 Synthesis of S4



2,3,5,6-tetrafluorophenol (500 mg, 3.01 mmol, 1 eq.), propargyl bromide (80% in toluene, 0.27 mL, 3.01 mmol, 1 eq.) and potassium carbonate (420 mg, 3.01 mmol, 1 eq.) were added to acetonitrile (15 mL) and the mixture stirred at 60 °C for 8 h. After cooling to room temperature, the mixture was washed with water (10 mL) and extracted thoroughly with ethyl acetate (4 x 20 mL). The combined

organic layers were dried over sodium sulphate, filtered, and condensed to give the crude product as an orange liquid. Purification was carried out via column chromatography (SiO<sub>2</sub>, PE/EtOAc : 10/1) to give the product as a yellow liquid (490 mg, 2.40 mmol, 80% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.84 (tt,  $J$  = 9.9, 7.0 Hz, 1H, H<sub>a</sub>), 4.88 (d,  $J$  = 2.3 Hz, 2H, H<sub>e</sub>), 2.56 (t,  $J$  = 2.4 Hz, 1H, H<sub>g</sub>).

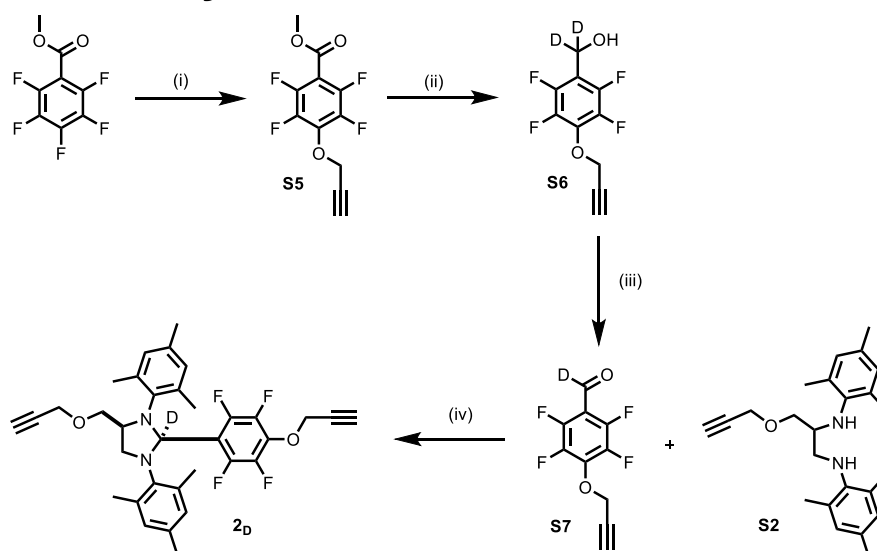
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 146.36 (dtd,  $J$  = 247.4, 12.5, 4.2 Hz, C<sub>b</sub>), 141.72 (dddd,  $J$  = 248.0, 15.0, 4.3, 3.3 Hz, C<sub>c</sub>), 136.36 (tt,  $J$  = 12.3, 3.6 Hz, C<sub>d</sub>), 100.83 (t,  $J$  = 23.1 Hz, C<sub>a</sub>), 77.38 (C<sub>f</sub>), 77.09 (C<sub>g</sub>), 61.68 (t,  $J$  = 3.9 Hz, C<sub>e</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -139.70 – -139.82 (m, 2F, F<sub>b</sub>), -155.57 – -155.71 (m, 2F, F<sub>c</sub>).

**MS-ESI(-)**:  $m/z$  = 165.0 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

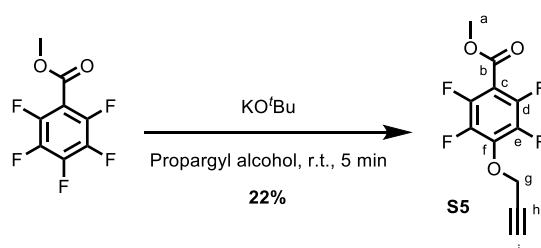
**MS-APCI(-)**:  $m/z$  = 165.1 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

### 3.3 Synthetic Route to 2<sub>D</sub>



**Figure 2.** Synthetic route to 2<sub>D</sub>. Conditions: (i) KO<sup>t</sup>Bu, propargyl alcohol, r.t., 5 min, 22% yield; (ii) NaBD<sub>4</sub>, THF/EtOH, r.t., 24 h, 78% yield; (iii) PCC, DCM, 0 °C, 1 h, 71% yield; (iv) acetic acid, r.t., 30 min, 57% yield.

#### 3.3.1 Synthesis of S5



Methyl pentafluorobenzoate (1.00 g, 4.42 mmol, 1 eq.) was dissolved in propargyl alcohol (10 mL). Potassium *tert*-butoxide (0.55 g, 4.87 mmol, 1.1 eq.) was separately dissolved in propargyl alcohol (10 mL) after which the mixture was added dropwise to the methyl pentafluorobenzoate solution. The reaction mixture was stirred for 5 min before being condensed to remove propargyl alcohol. DCM (30 mL) and water (30 mL) were added to the resulting solid. The organic phase was separated and dried over sodium sulphate before being condensed to give the crude product as a yellow liquid. Purification was carried out via column chromatography (SiO<sub>2</sub>, PE/EtOAc : 25/1) to give the product as a colourless liquid (0.25 g, 0.95 mmol, 22% yield).



**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 4.95 (s, 2H, H<sub>g</sub>), 3.95 (s, 3H, H<sub>a</sub>), 2.59 (t, *J* = 2.3 Hz, 1H, H<sub>i</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 160.28 (t, *J* = 2.6 Hz, C<sub>b</sub>), 145.62 (dddd, *J* = 256.9, 13.5, 6.9, 4.2 Hz, C<sub>d</sub>), 142.58 – 140.30 (m, C<sub>e</sub>), 138.40 (tt, *J* = 11.9, 3.7 Hz, C<sub>f</sub>), 107.10 (t, *J* = 15.6 Hz, C<sub>c</sub>), 77.90 (C<sub>i</sub>), 76.60 (C<sub>h</sub>), 61.69 (t, *J* = 4.2 Hz, C<sub>g</sub>), 53.27 (C<sub>a</sub>).

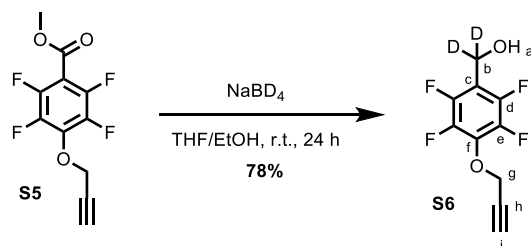
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -139.82 – -139.96 (m, 2F, F<sub>d</sub>), -155.03 – -155.19 (m, 2F, F<sub>e</sub>).

**MS-ESI(-)**: *m/z* = 223.0 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

**MS-APCI(+)**: *m/z* = 263.0 (30, [M+H]<sup>+</sup>).

**MS-APCI(-)**: *m/z* = 223.1 (100, [M-C<sub>8</sub>H<sub>3</sub>]<sup>-</sup>), 247.0 (5, [M-CH<sub>3</sub>]<sup>-</sup>).

### 3.3.2 Synthesis of S6



**S5** (250 mg, 0.95 mmol, 1 eq.) was dissolved in THF (3.8 mL) and ethanol (3.8 mL) and the mixture cooled in an ice bath. Sodium borodeuteride (56 mg, 1.34 mmol, 1.4 eq.) was added and the mixture placed under nitrogen before being stirred at room temperature for 24 h. Water (15 mL) was added before the mixture was condensed to remove THF and ethanol. The remaining aqueous residue was thoroughly extracted with ethyl acetate (3 x 20 mL). The combined organic phases were dried using sodium sulphate and condensed to give the crude product as a colourless liquid. Purification was carried out via column chromatography (SiO<sub>2</sub>, PE/EtOAc : 6/1) to give the pure product as a colourless liquid (175 mg, 0.74 mmol, 78% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ = 4.87 (d, *J* = 2.4 Hz, 2H, H<sub>g</sub>), 2.56 (t, *J* = 2.4 Hz, 1H, H<sub>i</sub>), 2.28 (br, 1H, H<sub>a</sub>).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ = 145.42 (dddd, *J* = 247.2, 12.5, 8.9, 4.1 Hz, C<sub>d</sub>), 141.56 (ddt, *J* = 248.7, 15.3, 3.9 Hz, C<sub>e</sub>), 135.73 (tt, *J* = 12.8, 3.7 Hz, C<sub>f</sub>), 113.23 (t, *J* = 18.1 Hz, C<sub>c</sub>), 77.47 (C<sub>h</sub>), 77.02 (C<sub>i</sub>), 61.68 (t, *J* = 3.9 Hz, C<sub>g</sub>), 52.81 – 52.11 (m, C<sub>b</sub>).

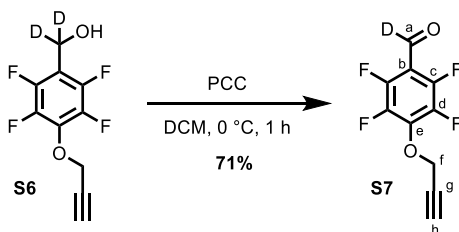
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -145.92 – -146.03 (m, 2F, F<sub>d</sub>), -155.73 – -155.86 (m, 2F, F<sub>e</sub>).

**<sup>2</sup>H NMR** (61 MHz, CHCl<sub>3</sub>) δ = 4.76 (s, 2D, D<sub>b</sub>).

**MS-ESI(-)**: *m/z* = 196.9 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

**MS-APCI(-)**: *m/z* = 197.0 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

### 3.3.3 Synthesis of S7



Pyridinium chlorochromate (460 mg, 2.12 mmol, 5 eq.) and molecular sieves (4 Å, 460 mg) were added to a microwave vial along with DCM (3.5 mL) before being placed under nitrogen and cooled in an ice bath. **S6** (100 mg, 0.42 mmol, 1 eq.) in DCM (0.5 mL) was added dropwise to the reaction

mixture under nitrogen. The mixture was stirred in an ice bath for 30 min before being allowed to warm to room temperature and stir for a further 30 min. The mixture was flushed through a silica plug (approx. 10 cm) using DCM. The collected solution was condensed to give the pure product as a colourless liquid (70 mg, 0.30 mmol, 71% yield).

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 5.03 (d,  $J$  = 2.2 Hz, 1H, H<sub>f</sub>), 2.61 (t,  $J$  = 2.4 Hz, 1H, H<sub>h</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 182.31 – 181.58 (m, C<sub>a</sub>), 147.70 (dddd,  $J$  = 262.3, 12.3, 7.1, 4.0 Hz, C<sub>c</sub>), 142.24 – 139.79 (m, C<sub>d</sub>), 140.98 (tt,  $J$  = 11.7, 4.2 Hz, C<sub>e</sub>), 110.27 – 109.90 (m, C<sub>b</sub>), 78.21 (C<sub>g</sub>), 76.38 (C<sub>h</sub>), 61.79 (t,  $J$  = 4.7 Hz, C<sub>f</sub>).

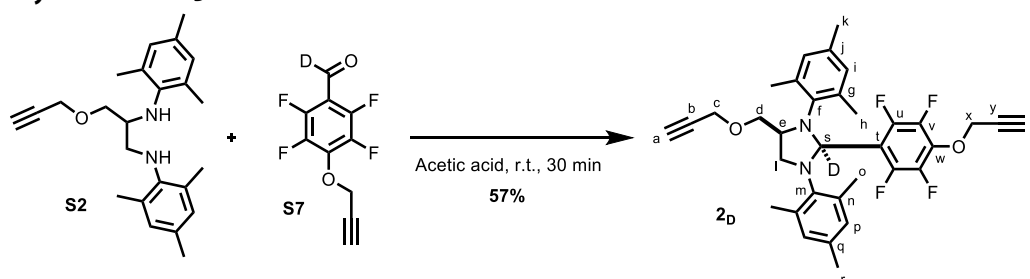
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -145.75 – -145.88 (m, 2F, F<sub>c</sub>), -155.29 – -155.43 (m, 2F, F<sub>d</sub>).

**<sup>2</sup>H NMR** (77 MHz, CHCl<sub>3</sub>)  $\delta$  = 10.28 (s, 1D, D<sub>a</sub>).

**MS-ESI(+)**:  $m/z$  = 203.0 (100, [M-CDO]<sup>+</sup>).

**MS-APCI(-)**:  $m/z$  = 194.1 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

### 3.3.4 Synthesis of 2<sub>D</sub>



**S2** (50 mg, 137  $\mu$ mol, 1 eq.) was dissolved in minimum acetic acid (approx. 0.2 mL). The solution was added to **S7** (48 mg, 206  $\mu$ mol, 1.5 eq.) and the mixture stirred for 30 min. The resulting brown precipitate was filtered off and washed thoroughly with ice-cold methanol to give the pure product as a white solid (45 mg, 78  $\mu$ mol, 57% yield).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.90 (s, 1H, H<sub>i</sub>), 6.76 (s, 2H, H<sub>p</sub>), 6.74 (s, 1H, H<sub>i</sub>), 4.77 (t,  $J$  = 2.7 Hz, 2H, H<sub>x</sub>), 4.16 (dd,  $J$  = 4.2, 2.4 Hz, 2H, H<sub>c</sub>), 4.01 (t,  $J$  = 8.8 Hz, 1H, H<sub>d</sub>), 3.91 (t,  $J$  = 8.1 Hz, 1H, H<sub>i</sub>), 3.83 (dddd,  $J$  = 9.4, 7.0, 4.1, 2.2 Hz, 1H, H<sub>e</sub>), 3.71 – 3.65 (m, 2H, H<sub>i</sub>, H<sub>d</sub>), 2.53 (s, 3H, H<sub>h</sub>), 2.47 (t,  $J$  = 2.5 Hz, 1H, H<sub>z</sub>), 2.42 (t,  $J$  = 2.4 Hz, 1H, H<sub>a</sub>), 2.50 – 2.26 (br, 6H, H<sub>o</sub>), 2.23 (s, 3H, H<sub>k</sub>), 2.19 (s, 3H, H<sub>r</sub>), 1.99 (s, 3H, H<sub>h</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 147.82 – 144.79 (m, C<sub>u</sub>), 142.93 – 139.33 (m, C<sub>v</sub>), 140.43 (C<sub>g</sub>), 140.03 (C<sub>f</sub>), 139.41 – 138.93 (br, C<sub>n</sub>), 137.61 (C<sub>m</sub>), 137.11 (C<sub>g</sub>), 137.19 – 136.77 (br, C<sub>n</sub>), 136.38 (C<sub>j</sub>), 135.42 (C<sub>q</sub>), 134.95 (t,  $J$  = 13.1 Hz, C<sub>w</sub>), 131.09 (C<sub>i</sub>), 130.78 – 130.24 (br, C<sub>p</sub>), 130.19 – 129.68 (br, C<sub>p</sub>), 129.51 (C<sub>i</sub>), 115.13 (t,  $J$  = 11.0 Hz, C<sub>t</sub>), 79.95 (C<sub>b</sub>), 77.21 (C<sub>z</sub>), 77.06 (C<sub>y</sub>), 74.54 (C<sub>a</sub>), 73.58 – 73.02 (m, C<sub>s</sub>), 73.10 (C<sub>d</sub>), 62.59 (C<sub>e</sub>), 61.52 (t,  $J$  = 3.7 Hz, C<sub>x</sub>), 58.58 (C<sub>c</sub>), 53.92 (C<sub>i</sub>), 20.89 (C<sub>k</sub>), 20.76 (C<sub>r</sub>), 20.48 – 19.96 (br, C<sub>o</sub>), 20.22 (C<sub>h</sub>), 18.79 – 18.33 (br, C<sub>o</sub>), 18.31 (C<sub>h</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -137.39 (dd,  $J$  = 21.5, 9.5 Hz, H<sub>u</sub>), -148.22 (dd,  $J$  = 22.5, 8.6 Hz, H<sub>u</sub>), -156.96 (dd,  $J$  = 20.9, 8.7 Hz, H<sub>v</sub>), -157.11 (dd,  $J$  = 22.2, 9.4 Hz, H<sub>v</sub>).

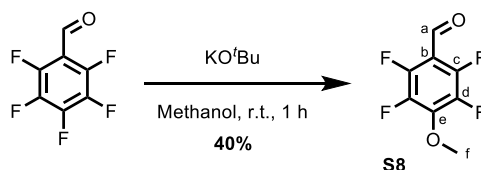
**<sup>2</sup>H NMR** (77 MHz, CHCl<sub>3</sub>)  $\delta$  = 6.33 (s, 1H, D<sub>s</sub>).

**MS-ESI(+)**:  $m/z$  = 618.2 (30, [M+K]<sup>+</sup>).

**HRMS-ESI(+)**: 618.2237 [M+K]<sup>+</sup>, calculated for C<sub>34</sub>H<sub>33</sub>DF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>K<sup>+</sup>: 618.2251.

### 3.4 Synthesis of S9

#### 3.4.1 Synthesis of S8



2,3,4,5,6-pentafluorobenzaldehyde (0.5 g, 2.55 mmol, 1 eq.) was dissolved in methanol (10 mL). Potassium *tert*-butoxide (0.32 g, 2.81 mmol, 1.1 eq.) was separately dissolved in methanol (10 mL) after which the mixture was added dropwise to the 2,3,4,5,6-pentafluorobenzaldehyde solution. The reaction mixture was stirred for 1 h before being condensed to remove methanol. DCM (20 mL) and water (20 mL) were added to the resulting solid. The organic phase was separated and dried over sodium sulphate before being condensed to give the crude product as a yellow liquid. Purification was carried out via column chromatography (SiO<sub>2</sub>, PE/EtOAc : 25/1) to give the product as a colourless liquid (0.21 g, 1.01 mmol, 40% yield).

**<sup>1</sup>H NMR** (500 MHz, CHCl<sub>3</sub>)  $\delta$  = 10.20 (s, 1H, H<sub>a</sub>), 4.22 (t,  $J$  = 2.2 Hz, 3H, H<sub>f</sub>).

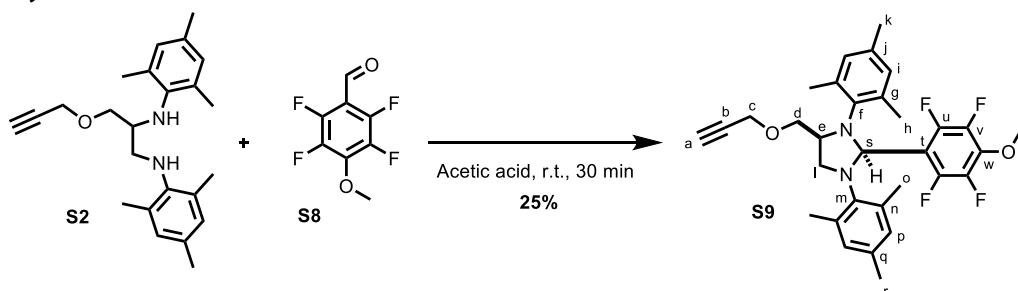
**<sup>13</sup>C NMR** (126 MHz, CHCl<sub>3</sub>)  $\delta$  = 182.30 (p,  $J$  = 3.0 Hz, C<sub>a</sub>), 147.87 (dddd,  $J$  = 260.8, 12.6, 7.2, 3.5 Hz, C<sub>c</sub>), 143.75 (tt,  $J$  = 10.8, 4.2 Hz, C<sub>e</sub>), 140.03 (ddt,  $J$  = 249.6, 14.6, 4.0 Hz, C<sub>d</sub>), 108.78 (t,  $J$  = 9.9 Hz, C<sub>b</sub>), 62.23 – 62.10 (m, C<sub>f</sub>).

**<sup>19</sup>F NMR** (376 MHz, CHCl<sub>3</sub>)  $\delta$  = -146.10 – -146.22 (m, 2F, F<sub>c</sub>), -157.98 – -158.18 (m, 2F, F<sub>d</sub>).

**MS-ESI(+)**:  $m/z$  = 179.0 (100, [M-CHO]<sup>+</sup>), 239.1 (20, [M-CH<sub>3</sub>+2Na]<sup>+</sup>).

**MS-APCI(-)**:  $m/z$  = 193.0 (100, [M-CH<sub>3</sub>]<sup>-</sup>).

#### 3.4.2 Synthesis of S9



**S2** (100 mg, 270  $\mu$ mol, 1 eq.) was dissolved in minimum acetic acid (approx. 0.3 mL). The solution was added to **S8** (57 mg, 270  $\mu$ mol, 1 eq.) and the mixture stirred for 30 min. The resulting brown precipitate was filtered off and washed thoroughly with ice-cold methanol to give the pure product as a white solid (38 mg, 69  $\mu$ mol, 25% yield).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 6.90 (s, 1H, H<sub>i</sub>), 6.76 (s, 2H, H<sub>p</sub>), 6.75 (s, 1H, H<sub>i</sub>), 6.33 (s, 1H, H<sub>s</sub>), 4.16 (dd,  $J$  = 4.1, 2.4 Hz, 2H, H<sub>c</sub>), 4.01 (t,  $J$  = 8.9 Hz, 1H, H<sub>d</sub>), 3.97 (s, 3H, H<sub>x</sub>), 3.90 (t,  $J$  = 8.2 Hz, 1H, H<sub>i</sub>), 3.85 – 3.79 (m, 1H, H<sub>e</sub>), 3.69 – 3.65 (m, 2H, H<sub>i</sub>, H<sub>a</sub>), 2.53 (s, 3H, H<sub>h</sub>), 2.50 – 2.29 (m, 6H, H<sub>o</sub>), 2.42 (t,  $J$  = 2.4 Hz, 1H, H<sub>a</sub>), 2.22 (s, 3H, H<sub>k</sub>), 2.19 (s, 3H, H<sub>r</sub>), 2.00 (s, 3H, H<sub>h</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>)  $\delta$  = 148.21 – 144.86 (m, C<sub>u</sub>), 142.17 – 138.55 (m, C<sub>v</sub>), 140.44 (C<sub>g</sub>), 140.11 (C<sub>f</sub>), 139.46 – 139.03 (br, C<sub>n</sub>), 137.73 (C<sub>m</sub>), 137.74 – 137.58 (m, C<sub>w</sub>), 137.30 – 136.69 (br, C<sub>n</sub>), 136.96

(C<sub>g</sub>), 136.33 (C<sub>i</sub>), 135.39 (C<sub>q</sub>), 131.10 (C<sub>i</sub>), 130.89 – 130.33 (br, C<sub>p</sub>), 130.21 – 129.69 (br, C<sub>p</sub>), 129.53 (C<sub>i</sub>), 113.42 (t, *J* = 11.0 Hz, C<sub>i</sub>), 79.97 (C<sub>b</sub>), 74.52 (C<sub>a</sub>), 73.52 (C<sub>s</sub>), 73.13 (C<sub>d</sub>), 62.53 (C<sub>e</sub>), 61.96 (t, *J* = 3.8 Hz, C<sub>x</sub>), 58.58 (C<sub>c</sub>), 53.87 (C<sub>i</sub>), 20.88 (C<sub>k</sub>), 20.77 (C<sub>r</sub>), 20.48 – 19.96 (br, C<sub>o</sub>), 20.26 (C<sub>h</sub>), 18.80 – 18.42 (br, C<sub>o</sub>), 18.37 (C<sub>h</sub>).

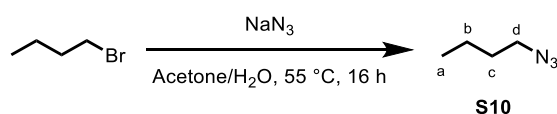
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>)  $\delta$  = -137.68 (dd, *J* = 20.5, 9.2 Hz), -148.51 (dd, *J* = 21.6, 8.4 Hz), -159.18 (dd, *J* = 21.6, 9.0 Hz), -159.32 (dd, *J* = 20.4, 8.4 Hz).

**MS-ESI(+)**: *m/z* = 555.3 (15, [M+H]<sup>+</sup>), 577.2 (90, [M+Na]<sup>+</sup>), 593.2 (90, [M+K]<sup>+</sup>), 375.2 (90, [M-C<sub>7</sub>H<sub>3</sub>F<sub>4</sub>O]<sup>+</sup>).

**HRMS-ESI(+)**: 593.2167 [M+K]<sup>+</sup>, calculated for C<sub>32</sub>H<sub>34</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub>K<sup>+</sup>: 593.2188.

### 3.5 Synthesis and Reactions of Imidazolinium Salts

#### 3.5.1 Synthesis of S10

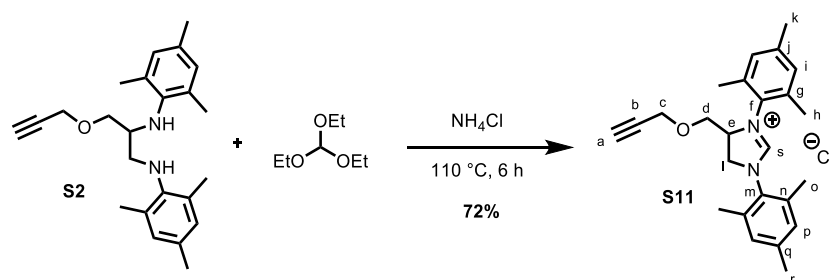


1-bromobutane (0.79 mL, 7.30 mmol, 1 eq.) was dissolved in acetone (8 mL) and water (4 mL). Sodium azide (0.71 g, 11.0 mmol, 1.5 eq.) was added and the mixture was stirred at 55 °C for 16 h. The mixture was cooled to room temperature before being thoroughly extracted with diethyl ether (3 x 15 mL). The combined organic extracts were dried over sodium sulfate and carefully condensed to give the crude product, as a light yellow liquid, which was used without further purification.

**<sup>1</sup>H NMR** (500 MHz, CHCl<sub>3</sub>)  $\delta$  = 3.26 (t, *J* = 7.0 Hz, 2H, H<sub>d</sub>), 1.62 – 1.55 (m, 2H, H<sub>c</sub>), 1.45 – 1.36 (m, 2H, H<sub>b</sub>), 0.94 (t, *J* = 7.4 Hz, 3H, H<sub>a</sub>).

**<sup>13</sup>C NMR** (126 MHz, CHCl<sub>3</sub>)  $\delta$  = 51.32 (C<sub>d</sub>), 31.00 (C<sub>c</sub>), 20.05 (C<sub>b</sub>), 13.75 (C<sub>a</sub>).

#### 3.5.2 Synthesis of S11



**S2** (100 mg, 0.27 mmol, 1 eq.) and NH<sub>4</sub>Cl (16 mg, 0.302 mmol, 1.1 eq.) were dissolved in triethyl orthoformate (137  $\mu$ L, 0.82 mmol, 3 eq.) and the solution placed in a sealed microwave vial. The mixture was heated to 110 °C for 6 h. After being cooled to room temperature, diethyl ether (15 mL) was added to precipitate the product. The diethyl ether was carefully decanted off and the remaining product dried thoroughly. No further purification was required; the product was a light brown powder (81 mg, 0.20 mmol, 72% yield).

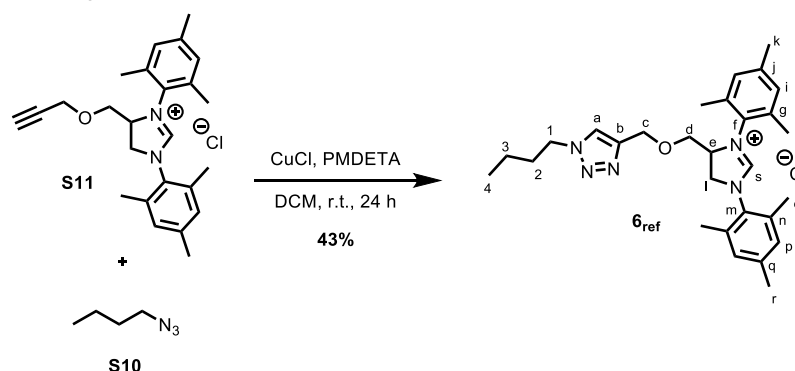
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.76 (s, 1H, H<sub>s</sub>), 6.96 (s, 2H, H<sub>i</sub> or H<sub>p</sub>), 6.95 (s, 2H, H<sub>i</sub> or H<sub>p</sub>), 5.47 (dt, *J* = 12.6, 4.6 Hz, 1H, H<sub>e</sub>), 4.93 (t, *J* = 12.2 Hz, 1H, H<sub>l</sub>), 4.38 (dd, *J* = 11.9, 7.3 Hz, 1H, H<sub>l</sub>), 4.22 (d, *J* = 2.3 Hz, 2H, H<sub>c</sub>), 3.82 (dd, *J* = 11.1, 2.3 Hz, 1H, H<sub>d</sub>), 3.59 (dd, *J* = 11.1, 1.6 Hz, 1H, H<sub>d</sub>), 2.44 (s, 4H, H<sub>a</sub>, H<sub>h</sub> or H<sub>o</sub>), 2.41 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.37 (s, 6H, H<sub>h</sub> or H<sub>o</sub>), 2.29 (s, 6H, H<sub>k</sub>, H<sub>r</sub>).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  = 158.92 ( $\text{C}_s$ ), 140.73 ( $\text{C}_j$  or  $\text{C}_q$ ), 140.48 ( $\text{C}_j$  or  $\text{C}_q$ ), 136.03 ( $\text{C}_g$  or  $\text{C}_n$ ), 135.50 ( $\text{C}_g$  or  $\text{C}_n$ ), 135.42 (br,  $\text{C}_g$  or  $\text{C}_n$ ), 135.35 (br,  $\text{C}_g$  or  $\text{C}_n$ ), 130.64 ( $\text{C}_i$  or  $\text{C}_p$ ), 130.41 ( $\text{C}_f$  or  $\text{C}_m$ ), 130.35 ( $\text{C}_i$  or  $\text{C}_p$ ), 130.14 ( $\text{C}_i$  or  $\text{C}_p$ ), 128.43 ( $\text{C}_f$  or  $\text{C}_m$ ), 78.18 ( $\text{C}_b$ ), 75.98 ( $\text{C}_a$ ), 66.64 ( $\text{C}_d$ ), 64.02 ( $\text{C}_e$ ), 58.63 ( $\text{C}_c$ ), 53.35 ( $\text{C}_l$ ), 21.19 ( $\text{C}_k$  or  $\text{C}_r$ ), 21.12 ( $\text{C}_k$  or  $\text{C}_r$ ), 19.06 ( $\text{C}_h$  or  $\text{C}_o$ ), 18.26 (br,  $\text{C}_h$  or  $\text{C}_o$ ), 18.00 ( $\text{C}_h$  or  $\text{C}_o$ ), 17.93 (br,  $\text{C}_h$  or  $\text{C}_o$ ).

**MS-ESI(+)**:  $m/z$  = 375.3 (100,  $[\text{M}-\text{Cl}]^+$ ).

**HRMS-ESI(+)**: 375.2420  $[\text{M}-\text{Cl}]^+$ , calculated for  $\text{C}_{25}\text{H}_{31}\text{ON}_2^+$ : 375.2431.

### 3.5.3 Synthesis of **6<sub>ref</sub>**



**S11** (50 mg, 122  $\mu\text{mol}$ , 1.00 eq.) and **S10** (60 mg, 608  $\mu\text{mol}$ , 5.00 eq.) were dissolved in DCM (0.5 mL) and placed in a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was placed PMDETA (2 mg, 120  $\mu\text{mol}$ , 0.10 eq.) and DCM (0.5 mL); this solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula into a third sealed microwave vial containing copper(I) chloride (1 mg, 6  $\mu\text{mol}$ , 0.05 eq.). This mixture was stirred until all the copper(I) chloride had dissolved at which point the mixture was degassed again via a single freeze-thaw-pump cycle. The copper-containing mixture was then transferred via cannula onto the solution containing **S11** and **S10**. The resulting solution was stirred for 24 h and then condensed to give the crude product. Purification was carried out via preparative TLC (DCM/methanol : 20/1,  $R_f$  = 0.1) to give the product as a colourless oil (27 mg, 53  $\mu\text{mol}$ , 43% yield).

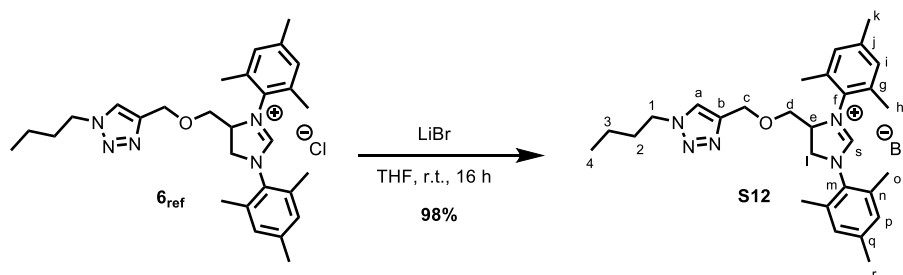
**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 8.47 (s, 1H,  $\text{H}_s$ ), 7.77 (s, 1H,  $\text{H}_a$ ), 6.97 (s, 2H,  $\text{H}_i$  or  $\text{H}_p$ ), 6.93 (s, 1H,  $\text{H}_i$  or  $\text{H}_p$ ), 6.92 (s, 1H,  $\text{H}_i$  or  $\text{H}_p$ ), 5.39 (dd,  $J$  = 12.5, 7.4 Hz, 1H,  $\text{H}_e$ ), 4.83 (t,  $J$  = 12.3 Hz, 1H,  $\text{H}_l$ ), 4.77 – 4.67 (m, 2H,  $\text{H}_c$ ), 4.47 (dd,  $J$  = 12.1, 7.2 Hz, 1H,  $\text{H}_l$ ), 4.37 (t,  $J$  = 7.3 Hz, 2H,  $\text{H}_1$ ), 4.01 (dd,  $J$  = 11.2, 2.4 Hz, 1H,  $\text{H}_d$ ), 3.59 (d,  $J$  = 11.0 Hz, 1H,  $\text{H}_d$ ), 2.44 (s, 3H,  $\text{H}_h$  or  $\text{H}_o$ ), 2.43 (s, 3H,  $\text{H}_h$  or  $\text{H}_o$ ), 2.34 (br, 3H,  $\text{H}_h$  or  $\text{H}_o$ ), 2.30 (s, 3H,  $\text{H}_k$  or  $\text{H}_r$ ), 2.29 (s, 3H,  $\text{H}_k$  or  $\text{H}_r$ ), 2.19 (br, 3H,  $\text{H}_h$  or  $\text{H}_o$ ), 1.90 (p,  $J$  = 7.4 Hz, 2H,  $\text{H}_2$ ), 1.35 (h,  $J$  = 7.4 Hz, 2H,  $\text{H}_3$ ), 0.96 (t,  $J$  = 7.4 Hz, 3H,  $\text{H}_4$ ).

**$^{13}\text{C}$  NMR** (126 MHz,  $\text{CDCl}_3$ )  $\delta$  = 158.49 ( $\text{C}_s$ ), 143.11 ( $\text{C}_b$ ), 140.83 ( $\text{C}_j$  or  $\text{C}_q$ ), 140.61 ( $\text{C}_j$  or  $\text{C}_q$ ), 136.21 ( $\text{C}_g$  or  $\text{C}_n$ ), 135.63 (br,  $\text{C}_g$  or  $\text{C}_n$ ), 135.34 (br,  $\text{C}_g$  or  $\text{C}_n$ ), 135.06 (br,  $\text{C}_g$  or  $\text{C}_n$ ), 130.60 ( $\text{C}_i$  or  $\text{C}_p$ ), 130.45 ( $\text{C}_i$  or  $\text{C}_p$ ), 130.32 ( $\text{C}_f$  or  $\text{C}_m$ ), 130.18 (br,  $\text{C}_i$  or  $\text{C}_p$ ), 130.10 (br,  $\text{C}_i$  or  $\text{C}_p$ ), 128.47 ( $\text{C}_f$  or  $\text{C}_m$ ), 123.58 ( $\text{C}_a$ ), 66.97 ( $\text{C}_d$ ), 64.40 ( $\text{C}_e$ ), 64.33 ( $\text{C}_c$ ), 53.42 ( $\text{C}_l$ ), 50.28 ( $\text{C}_1$ ), 32.42 ( $\text{C}_2$ ), 21.20 ( $\text{C}_k$  or  $\text{C}_r$ ), 21.15 ( $\text{C}_k$  or  $\text{C}_r$ ), 19.85 ( $\text{C}_3$ ), 18.90 ( $\text{C}_h$  or  $\text{C}_o$ ), 18.12 (br,  $\text{C}_h$  or  $\text{C}_o$ ), 17.89 ( $\text{C}_h$  or  $\text{C}_o$ ), 17.73 (br,  $\text{C}_h$  or  $\text{C}_o$ ), 13.62 ( $\text{C}_4$ ).

**MS-ESI(+)**:  $m/z$  = 474.4 (100,  $[\text{M}-\text{Cl}]^+$ ).

**HRMS-ESI(+)**: 474.3217  $[\text{M}-\text{Cl}]^+$ , calculated for  $\text{C}_{29}\text{H}_{40}\text{ON}_5^+$ : 474.3227.

### 3.5.4 Synthesis of S12



**6<sub>ref</sub>** (10 mg, 20  $\mu$ mol, 1 eq.) was dissolved in THF (2 mL) and LiBr (35 mg, 400  $\mu$ mol, 20 eq.) was added. The mixture was stirred for 16 h before being condensed to remove the solvent. The crude product was then dissolved in DCM and filtered to remove remaining salt species before being condensed to give the pure product as a colourless oil (11 mg, 19  $\mu$ mol, 98% yield).

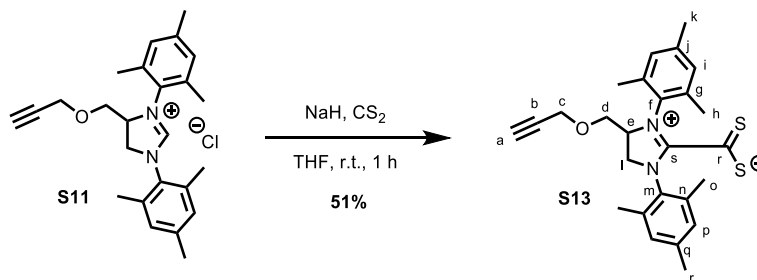
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 8.18 (s, 1H, H<sub>s</sub>), 7.78 (s, 1H, H<sub>a</sub>), 6.97 (s, 2H, H<sub>i</sub> or H<sub>p</sub>), 6.94 – 6.90 (m, 2H, H<sub>i</sub> or H<sub>p</sub>), 5.50 – 5.41 (m, 1H, H<sub>e</sub>), 4.90 (t, *J* = 12.3 Hz, 1H, H<sub>i</sub>), 4.78 – 4.64 (m, 2H, H<sub>c</sub>), 4.46 (dd, *J* = 12.1, 7.4 Hz, 1H, H<sub>i</sub>), 4.37 (t, *J* = 7.3 Hz, 2H, H<sub>1</sub>), 4.01 (dd, *J* = 11.3, 2.5 Hz, 1H, H<sub>d</sub>), 3.58 (dd, *J* = 11.3, 1.5 Hz, 1H, H<sub>d</sub>), 2.44 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.42 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.34 (br, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.30 (s, 3H, H<sub>k</sub> or H<sub>r</sub>), 2.29 (s, 3H, H<sub>k</sub> or H<sub>r</sub>), 2.18 (br, 3H, H<sub>h</sub> or H<sub>o</sub>), 1.93 – 1.86 (m, 2H, H<sub>2</sub>), 1.39 – 1.30 (m, 2H, H<sub>3</sub>), 0.96 (t, *J* = 7.4 Hz, 3H, H<sub>4</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 157.89 (C<sub>s</sub>), 143.02 (C<sub>b</sub>), 140.90 (C<sub>j</sub> or C<sub>q</sub>), 140.69 (C<sub>j</sub> or C<sub>q</sub>), 136.12 (C<sub>g</sub> or C<sub>n</sub>), 135.55 (br, C<sub>g</sub> or C<sub>n</sub>), 135.46 (C<sub>g</sub> or C<sub>n</sub>), 135.07 (br, C<sub>g</sub> or C<sub>n</sub>), 130.65 (C<sub>i</sub> or C<sub>p</sub>), 130.41 (C<sub>i</sub> or C<sub>p</sub>), 130.23 (C<sub>f</sub> or C<sub>m</sub>), 130.15 (br, C<sub>i</sub> or C<sub>p</sub>), 128.36 (C<sub>f</sub> or C<sub>m</sub>), 123.64 (C<sub>a</sub>), 66.85 (C<sub>d</sub>), 64.51 (C<sub>e</sub>), 64.30 (C<sub>c</sub>), 53.56 (C<sub>l</sub>), 50.27 (C<sub>1</sub>), 32.41 (C<sub>2</sub>), 21.20 (C<sub>k</sub> or C<sub>r</sub>), 21.14 (C<sub>k</sub> or C<sub>r</sub>), 19.84 (C<sub>3</sub>), 19.09 (C<sub>h</sub> or C<sub>o</sub>), 18.24 (br, C<sub>h</sub> or C<sub>o</sub>), 17.87 (C<sub>h</sub> or C<sub>o</sub>), 17.72 (br, C<sub>h</sub> or C<sub>o</sub>), 13.62 (C<sub>4</sub>).

**MS-ESI(+):**  $m/z = 474.4$  (100,  $[M-Br]^+$ ).

**HRMS-ESI(+):** 474.3228 [M-Br]<sup>+</sup>, calculated for C<sub>29</sub>H<sub>40</sub>ON<sub>5</sub><sup>+</sup>: 474.3227.

### 3.5.5 Synthesis of S13



**S11** (50 mg, 122  $\mu\text{mol}$ , 1.0 eq.) and  $\text{CS}_2$  (147  $\mu\text{L}$ , 244  $\mu\text{mol}$ , 20.0 eq.) were dissolved in dry THF (5 mL). NaH (60% in mineral oil, 5 mg, 134  $\mu\text{mol}$ , 1.1 eq.) was added and the mixture stirred for 1 h.  $\text{H}_2\text{O}$  (0.05 mL) was added before the solution was washed with brine. The organic phase was separated, dried over sodium sulfate, and condensed to give the crude product. The crude product was dissolved in minimal DCM before a large quantity of diethyl ether was added to precipitate the pure product as a dark red solid that was collected by filtration (28 mg, 62  $\mu\text{mol}$ , 51% yield).

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 6.88 (s, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.86 (s, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.85 (s, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.83 (s, 1H, H<sub>i</sub> or H<sub>p</sub>), 4.54 (ddt, *J* = 11.5, 7.7, 3.8 Hz, 1H, H<sub>e</sub>), 4.33 – 4.18 (m, 4H, H<sub>c</sub>+H<sub>i</sub>), 3.75 (dd, *J* = 10.1, 4.3

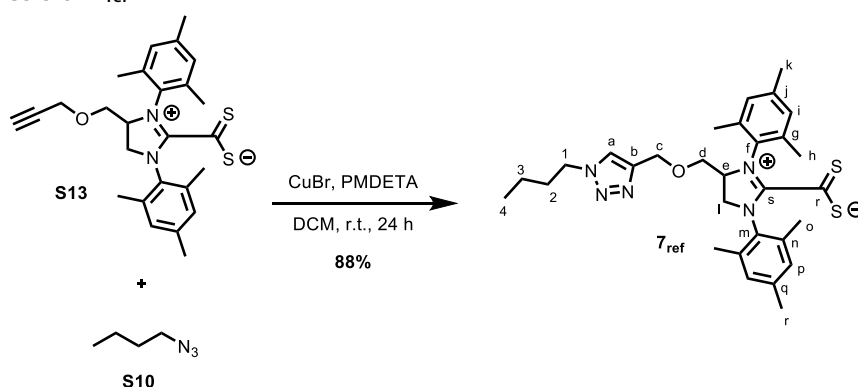
Hz, 1H, H<sub>d</sub>), 3.65 (dd, *J* = 10.1, 3.3 Hz, 1H, H<sub>d</sub>), 2.57 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.55 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.51 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.50 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.48 (t, *J* = 2.4 Hz, 1H, H<sub>a</sub>), 2.23 (s, 3H, H<sub>k</sub> or H<sub>r</sub>), 2.22 (s, 3H, H<sub>k</sub> or H<sub>r</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 222.34 (C<sub>t</sub>), 164.31 (C<sub>s</sub>), 139.83 (C<sub>j</sub> or C<sub>q</sub>), 139.72 (C<sub>j</sub> or C<sub>q</sub>), 138.19 (C<sub>g</sub> or C<sub>n</sub>), 137.12 (C<sub>g</sub> or C<sub>n</sub>), 136.36 (C<sub>g</sub> or C<sub>n</sub>), 136.31 (C<sub>g</sub> or C<sub>n</sub>), 130.62 (C<sub>f</sub> or C<sub>m</sub>), 130.29 (C<sub>i</sub> or C<sub>p</sub>), 130.11 (C<sub>i</sub> or C<sub>p</sub>), 129.94 (C<sub>f</sub> or C<sub>m</sub>), 129.87 (C<sub>i</sub> or C<sub>p</sub>), 129.80 (C<sub>i</sub> or C<sub>p</sub>), 78.47 (C<sub>b</sub>), 75.97 (C<sub>a</sub>), 67.40 (C<sub>d</sub>), 61.27 (C<sub>e</sub>), 58.70 (C<sub>c</sub>), 51.63 (C<sub>l</sub>), 21.11 (C<sub>k</sub> or C<sub>r</sub>), 21.08 (C<sub>k</sub> or C<sub>r</sub>), 19.48 (C<sub>h</sub> or C<sub>o</sub>), 19.37 (C<sub>h</sub> or C<sub>o</sub>), 18.96 (C<sub>h</sub> or C<sub>o</sub>), 18.84 (C<sub>h</sub> or C<sub>o</sub>).

**MS-ESI(+)**: *m/z* = 451.3 (50, [M+H]<sup>+</sup>), 473.3 (100, [M+Na]<sup>+</sup>).

**HRMS-ESI(+)**: 473.1696 [M+Na]<sup>+</sup>, calculated for C<sub>26</sub>H<sub>30</sub>ON<sub>2</sub>S<sub>2</sub>Na<sup>+</sup>: 473.1692.

### 3.5.6 Synthesis of 7<sub>ref</sub>



**S13** (15 mg, 36.5 μmol, 1.00 eq.), **S10** (18 mg, 182 μmol, 5.00 eq.), and PMDETA (1 μL, 4 μmol, 0.10 eq.) were dissolved in DCM (0.5 mL) and the solution added to a sealed microwave vial. The solution was thoroughly degassed via three freeze-thaw-pump cycles. In a separate microwave vial was added copper(I) bromide (0.3 mg, 2 μmol, 0.05 eq.) under nitrogen. The reaction mixture was transferred via cannula onto the copper(I) bromide and stirred for 24 h. The mixture was washed with aqueous EDTA solution (0.25 M, pH 7). The organic phase was separated, dried over sodium sulfate, and condensed to give the crude product which was left under high vacuum for 48 h. The product was found to be pure as a light yellow oil (16 mg, 31 μmol, 88% yield).

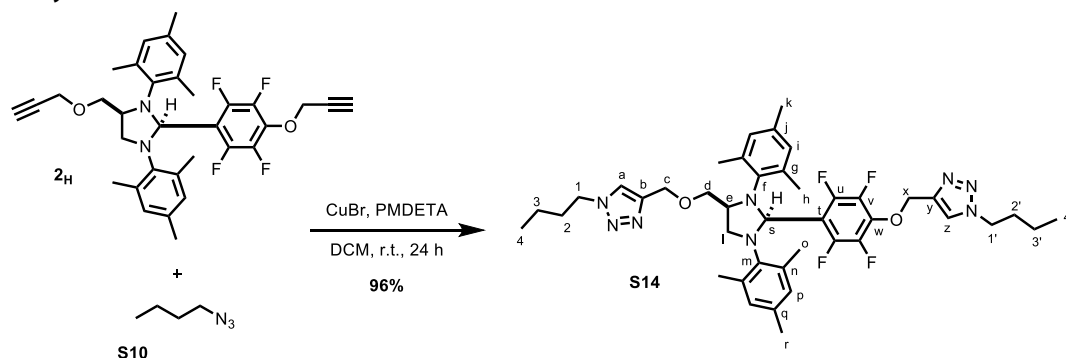
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ = 7.63 (s, 1H, H<sub>a</sub>), 6.89 (d, *J* = 2.0 Hz, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.84 (d, *J* = 2.0 Hz, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.82 (d, *J* = 1.8 Hz, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.80 (d, *J* = 1.8 Hz, 1H, H<sub>i</sub> or H<sub>p</sub>), 4.77 – 4.69 (m, 2H, H<sub>c</sub>), 4.50 (ddt, *J* = 10.7, 8.7, 3.3 Hz, 1H, H<sub>e</sub>), 4.38 (t, *J* = 7.2 Hz, 2H, H<sub>1</sub>), 4.24 – 4.20 (m, 2H, H<sub>1</sub>), 3.77 (dd, *J* = 10.3, 3.5 Hz, 1H, H<sub>d</sub>), 3.67 (dd, *J* = 10.4, 3.1 Hz, 1H, H<sub>d</sub>), 2.55 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.50 (s, 6H, H<sub>h</sub> or H<sub>o</sub>), 2.37 (s, 3H, H<sub>h</sub> or H<sub>o</sub>), 2.23 (s, 3H, H<sub>k</sub> or H<sub>r</sub>), 2.20 (s, 3H, H<sub>k</sub> or H<sub>r</sub>), 1.94 – 1.87 (m, 2H, H<sub>2</sub>), 1.42 – 1.33 (m, 2H, H<sub>3</sub>), 0.98 (t, *J* = 7.4 Hz, 3H, H<sub>4</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 222.48 (C<sub>t</sub>), 164.46 (C<sub>s</sub>), 143.91 (C<sub>b</sub>), 139.83 (C<sub>j</sub> or C<sub>q</sub>), 139.74 (C<sub>j</sub> or C<sub>q</sub>), 138.06 (C<sub>g</sub> or C<sub>n</sub>), 137.00 (C<sub>g</sub> or C<sub>n</sub>), 136.42 (C<sub>g</sub> or C<sub>n</sub>), 136.27 (C<sub>g</sub> or C<sub>n</sub>), 130.59 (C<sub>f</sub> or C<sub>m</sub>), 130.27 (C<sub>i</sub> or C<sub>p</sub>), 130.19 (C<sub>i</sub> or C<sub>p</sub>), 130.16 (C<sub>f</sub> or C<sub>m</sub>), 129.82 (C<sub>i</sub> or C<sub>p</sub>), 129.80 (C<sub>i</sub> or C<sub>p</sub>), 122.88 (C<sub>a</sub>), 68.39 (C<sub>d</sub>), 65.03 (C<sub>c</sub>), 61.52 (C<sub>e</sub>), 51.38 (C<sub>l</sub>), 50.35 (C<sub>1</sub>), 32.43 (C<sub>2</sub>), 21.09 (C<sub>k</sub> + C<sub>r</sub>), 19.87 (C<sub>3</sub>), 19.36 (C<sub>h</sub> or C<sub>o</sub>), 19.16 (C<sub>h</sub> or C<sub>o</sub>), 18.89 (C<sub>h</sub> or C<sub>o</sub>), 18.86 (C<sub>h</sub> or C<sub>o</sub>), 13.63 (C<sub>4</sub>).

**MS-ESI(+)**: *m/z* = 572.3 (100, [M+Na]<sup>+</sup>).

**HRMS-ESI(+)**: 572.2478 [M+Na]<sup>+</sup>, calculated for C<sub>30</sub>H<sub>39</sub>ON<sub>5</sub>S<sub>2</sub>Na<sup>+</sup>: 572.2488.

### 3.5.7 Synthesis of S14



**2H** (50 mg, 86  $\mu$ mol, 1.0 eq.), **S10** (86 mg, 864  $\mu$ mol, 10.0 eq.), and PMDETA (4  $\mu$ L, 17  $\mu$ mol, 0.2 eq.) were dissolved in DCM (2 mL) and the solution added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles before being transferred via cannula into another sealed microwave vial containing copper(I) bromide (1 mg, 9  $\mu$ mol, 0.1 eq.). The solution was stirred for 24 h before being washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species. The organic phases were then dried over sodium sulfate and condensed to give the crude product. This residue was dried under high vacuum for several days to give the pure product as a light yellow oil (64 mg, 83  $\mu$ mol, 96% yield).

**$^1\text{H}$  NMR** (500 MHz,  $\text{CHCl}_3$ )  $\delta$  = 7.54 (s, 1H,  $\text{H}_2$ ), 7.39 (s, 1H,  $\text{H}_a$ ), 6.88 (s, 1H,  $\text{H}_i$ ), 6.74 (s, 3H,  $\text{H}_i + \text{H}_p$ ), 6.30 (s, 1H,  $\text{H}_s$ ), 5.27 (s, 2H,  $\text{H}_x$ ), 4.64 (s, 2H,  $\text{H}_c$ ), 4.36 – 4.27 (m, 4H,  $\text{H}_1 + \text{H}_{1'}$ ), 3.94 (t,  $J$  = 8.1 Hz, 1H,  $\text{H}_d$ ), 3.89 – 3.82 (m, 2H,  $\text{H}_e$ ,  $\text{H}_l$ ), 3.71 (dd,  $J$  = 8.4, 3.5 Hz, 1H,  $\text{H}_d$ ), 3.66 (d,  $J$  = 6.4 Hz, 1H,  $\text{H}_l$ ), 2.51 (s, 3H,  $\text{H}_h$ ), 2.46 – 2.24 (br, 6H,  $\text{H}_o$ ), 2.22 (s, 3H,  $\text{H}_k$ ), 2.18 (s, 3H,  $\text{H}_r$ ), 1.96 (s, 3H,  $\text{H}_n$ ), 1.91 – 1.80 (m, 4H,  $\text{H}_2 + \text{H}_{2'}$ ), 1.40 – 1.26 (m, 4H,  $\text{H}_3 + \text{H}_{3'}$ ), 1.00 – 0.88 (m, 6H,  $\text{H}_4 + \text{H}_{4'}$ ).

**$^{13}\text{C}$  NMR** (126 MHz,  $\text{CHCl}_3$ )  $\delta$  = 147.69 – 145.09 (m,  $\text{C}_u$ ), 145.35 ( $\text{C}_b$ ), 142.97 ( $\text{C}_v$ ), 142.57 – 139.05 (m,  $\text{C}_v$ ), 140.47 ( $\text{C}_g$ ), 140.02 ( $\text{C}_f$ ), 139.03 (br,  $\text{C}_n$ ), 137.67 ( $\text{C}_m$ ), 136.92 ( $\text{C}_g$ ), 136.91 (br,  $\text{C}_n$ ), 136.26 ( $\text{C}_j$ ), 135.87 (t,  $J$  = 10.5 Hz,  $\text{C}_w$ ), 135.39 ( $\text{C}_q$ ), 131.03 ( $\text{C}_i$ ), 130.54 (br,  $\text{C}_p$ ), 129.94 (br,  $\text{C}_p$ ), 129.51 ( $\text{C}_i$ ), 123.00 ( $\text{C}_2$ ), 122.17 ( $\text{C}_a$ ), 114.71 (t,  $J$  = 11.0 Hz,  $\text{C}_t$ ), 73.71 ( $\text{C}_d$ ), 73.59 ( $\text{C}_s$ ), 67.72 (t,  $J$  = 3.4 Hz,  $\text{C}_x$ ), 65.04 ( $\text{C}_c$ ), 62.58 ( $\text{C}_e$ ), 53.92 ( $\text{C}_l$ ), 50.28 ( $\text{C}_1$  or  $\text{C}_{1'}$ ), 50.13 ( $\text{C}_1$  or  $\text{C}_{1'}$ ), 32.36 ( $\text{C}_2$  or  $\text{C}_{2'}$ ), 32.32 ( $\text{C}_2$  or  $\text{C}_{2'}$ ), 20.86 ( $\text{C}_k$ ), 20.74 ( $\text{C}_r$ ), 20.27 (br,  $\text{C}_o$ ), 20.20 ( $\text{C}_h$ ), 19.84 ( $\text{C}_3$  or  $\text{C}_{3'}$ ), 19.73 ( $\text{C}_3$  or  $\text{C}_{3'}$ ), 18.37 (br,  $\text{C}_o$ ), 18.31 ( $\text{C}_h$ ), 18.29 ( $\text{C}_h$ ), 13.58 ( $\text{C}_4$  or  $\text{C}_{4'}$ ), 13.51 ( $\text{C}_4$  or  $\text{C}_{4'}$ ).

**$^{19}\text{F}$  NMR** (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -137.11 – -137.26 (m, 1F,  $\text{F}_u$ ), -148.21 – -148.38 (m, 1F,  $\text{F}_u$ ), -157.25 (dd,  $J$  = 20.8, 8.5 Hz, 1F,  $\text{F}_v$ ), -157.34 (dd,  $J$  = 22.3, 9.4 Hz, 1F,  $\text{F}_v$ ).

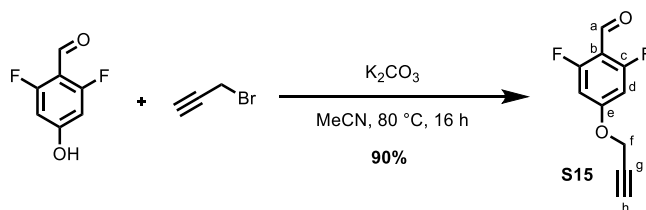
**MS-ESI(+)**:  $m/z$  = 799.6 (100,  $[\text{M}+\text{Na}]^+$ ).

**HRMS-ESI(+)**: 799.4040  $[\text{M}+\text{Na}]^+$ , calculated for  $\text{C}_{32}\text{H}_{34}\text{F}_4\text{N}_2\text{O}_2\text{K}^+$ : 799.4042.



### 3.6 Synthesis of Bis- and Mono-Fluorinated Mechanophores and Reference Compounds

#### 3.6.1 Synthesis of S15



2,6-difluoro-4-hydroxybenzaldehyde (500 mg, 3.16 mmol, 1 eq.) and propargyl bromide (80% in toluene, 0.28 mL, 3.16 mmol, 1 eq.) were dissolved in acetonitrile. Potassium carbonate (437 mg, 3.16 mmol, 1 eq.) was added and the mixture stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was washed with water (20 mL) and extracted thoroughly with DCM (4 x 20 mL). The combined organic layers were dried over sodium sulphate, filtered, and condensed to give the crude product as a light brown solid that required no further purification (564 mg, 2.85 mmol, 90% yield).

**<sup>1</sup>H NMR** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 10.20 (d, *J* = 1.1 Hz, 1H, H<sub>a</sub>), 6.71 – 6.52 (m, 2H, H<sub>d</sub>), 4.75 (d, *J* = 2.5 Hz, 2H, H<sub>f</sub>), 2.62 (t, *J* = 2.4 Hz, 1H, H<sub>h</sub>).

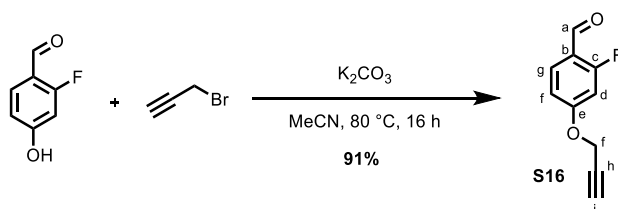
**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 183.58 – 183.49 (m, C<sub>a</sub>), 164.62 (dd, *J* = 261.6, 9.0 Hz, C<sub>c</sub>), 163.65 (t, *J* = 14.9 Hz, C<sub>e</sub>), 108.89 (t, *J* = 11.2 Hz, C<sub>b</sub>), 100.52 – 99.27 (m, C<sub>d</sub>), 77.53 (C<sub>h</sub>), 76.55 (C<sub>g</sub>), 56.80 (C<sub>f</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -112.59 (s, 2F, F<sub>c</sub>).

**MS-ESI(+)**: *m/z* = 219.0 (90, [M+Na]<sup>+</sup>), 197.0 (15, [M]<sup>+</sup>).

**HRMS-ESI(+)**: 219.0219 [M+Na]<sup>+</sup>, calculated for C<sub>10</sub>H<sub>6</sub>F<sub>2</sub>O<sub>2</sub>Na<sup>+</sup>: 219.0228.

#### 3.6.2 Synthesis of S16



2-fluoro-4-hydroxybenzaldehyde (500 mg, 3.57 mmol, 1 eq.) and propargyl bromide (80% in toluene, 0.32 mL, 3.57 mmol, 1 eq.) were dissolved in acetonitrile. Potassium carbonate (494 mg, 3.57 mmol, 1 eq.) was added and the mixture stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was washed with water (20 mL) and extracted thoroughly with DCM (4 x 20 mL). The combined organic layers were dried over sodium sulphate, filtered, and condensed to give the crude product as a light brown solid that required no further purification (579 mg, 3.25 mmol, 91% yield).

**<sup>1</sup>H NMR** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 10.22 (s, 1H, H<sub>a</sub>), 7.84 (t, *J* = 8.4 Hz, 1H, H<sub>d</sub>), 6.86 (dd, *J* = 8.8, 2.2 Hz, 1H, H<sub>g</sub>), 6.75 (dd, *J* = 12.1, 2.3 Hz, 1H, H<sub>f</sub>), 4.76 (d, *J* = 2.4 Hz, 2H, H<sub>h</sub>), 2.60 (t, *J* = 2.5 Hz, 1H, H<sub>i</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 186.02 (t, *J* = 5.3 Hz, C<sub>a</sub>), 166.14 (d, *J* = 258.8 Hz, C<sub>c</sub>), 163.95 (d, *J* = 11.8 Hz, C<sub>e</sub>), 130.29 (d, *J* = 3.8 Hz, C<sub>d</sub>), 118.63 (d, *J* = 8.4 Hz, C<sub>b</sub>), 111.97 (d, *J* = 2.7 Hz, C<sub>g</sub>), 102.74 (dd, *J* = 24.5, 3.1 Hz, C<sub>i</sub>), 77.03 (C<sub>i</sub> or C<sub>j</sub>), 76.96 (C<sub>i</sub> or C<sub>j</sub>), 56.48 (C<sub>h</sub>).

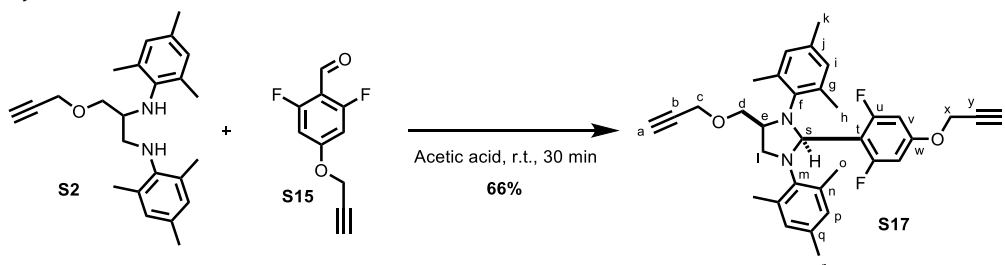
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -118.90 (s, 1F, F<sub>c</sub>).

**MS-ESI(+)**: m/z = 200.9 (40, [M+Na]<sup>+</sup>), 179.0 (15, [M]<sup>+</sup>).

**MS-ESI(-)**: m/z = 138.9 (100, [M-C<sub>3</sub>H<sub>3</sub>]<sup>-</sup>).

**HRMS-ESI(+)**: 201.0316 [M+Na]<sup>+</sup>, calculated for C<sub>10</sub>H<sub>7</sub>FO<sub>2</sub>Na<sup>+</sup>: 201.0322

### 3.6.3 Synthesis of S17



**S2** (100 mg, 0.27 mmol, 1 eq.) was dissolved in minimum acetic acid (approx. 0.3 mL). The solution was added to **S15** (53 mg, 0.27 mmol, 1 eq.) and the mixture stirred for 30 min. The resulting brown precipitate was filtered off and washed thoroughly with ice-cold methanol to give the pure product as a white solid (97 mg, 0.19 mmol, 66% yield).

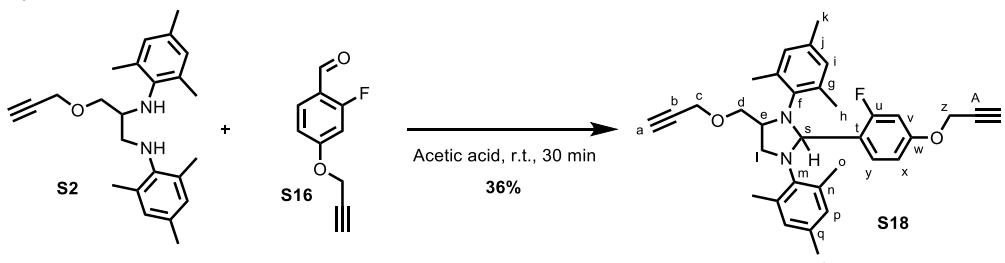
**<sup>1</sup>H NMR** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 6.89 (d, *J* = 2.3 Hz, 1H, H<sub>i</sub>), 6.76 – 6.69 (m, 3H, H<sub>i</sub> + H<sub>p</sub>), 6.39 (dt, *J* = 12.5, 2.1 Hz, 1H, H<sub>v</sub>), 6.30 (d, *J* = 1.9 Hz, 1H, H<sub>s</sub>), 6.11 (ddd, *J* = 12.0, 2.5, 1.4 Hz, 1H, H<sub>v</sub>), 4.51 (d, *J* = 2.4 Hz, 2H, H<sub>x</sub>), 4.16 (dd, *J* = 5.3, 2.4 Hz, 2H, H<sub>c</sub>), 4.07 – 4.01 (m, 1H, H<sub>d</sub>), 3.94 – 3.87 (m, 1H, H<sub>l</sub>), 3.82 – 3.77 (m, 1H, H<sub>e</sub>), 3.69 – 3.64 (m, 2H, H<sub>d</sub> + H<sub>l</sub>), 2.54 (s, 3H, H<sub>h</sub>), 2.53 – 2.31 (m, 6H, H<sub>o</sub>), 2.50 (t, *J* = 2.4 Hz, 1H, H<sub>z</sub>), 2.42 (t, *J* = 2.4 Hz, 1H, H<sub>a</sub>), 2.22 (s, 3H, H<sub>k</sub>), 2.18 (s, 3H, H<sub>r</sub>), 2.00 (s, 3H, H<sub>n</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 164.48 – 161.75 (m, C<sub>u</sub>), 158.13 (t, *J* = 14.8 Hz, C<sub>w</sub>), 140.86 (C<sub>g</sub>), 140.73 (C<sub>f</sub>), 139.31 (br, C<sub>n</sub>), 138.31 (C<sub>m</sub>), 137.24 (br, C<sub>n</sub>), 137.10 (C<sub>g</sub>), 135.91 (C<sub>j</sub>), 134.93 (C<sub>q</sub>), 130.88 (C<sub>i</sub>), 130.35 (br, C<sub>p</sub>), 129.71 (br, C<sub>p</sub>), 129.32 (C<sub>i</sub>), 110.33 (t, *J* = 12.8 Hz, C<sub>t</sub>), 100.16 (d, *J* = 26.1 Hz, C<sub>v</sub>), 97.76 (d, *J* = 28.2 Hz, C<sub>v</sub>), 80.12 (C<sub>b</sub>), 77.62 (d, *J* = 2.0 Hz, C<sub>y</sub>), 76.36 (d, *J* = 8.4 Hz, C<sub>z</sub>), 74.38 (d, *J* = 7.8 Hz, C<sub>a</sub>), 73.37 (C<sub>s</sub>), 73.01 (C<sub>d</sub>), 62.28 (C<sub>e</sub>), 58.53 (C<sub>c</sub>), 56.23 (C<sub>x</sub>), 53.60 (C<sub>i</sub>), 20.89 (d, *J* = 2.6 Hz, C<sub>k</sub>), 20.75 (d, *J* = 2.0 Hz, C<sub>r</sub>), 20.34 (C<sub>h</sub>), 20.30 (br, C<sub>o</sub>), 18.53 (br, C<sub>o</sub>), 18.45 (d, *J* = 2.7 Hz, C<sub>h</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -103.65 (d, *J* = 5.6 Hz, 1F, F<sub>u</sub>), -116.49 (d, *J* = 5.6 Hz, 1F, F<sub>u</sub>).

**HRMS-ESI(+)**: 543.2808 [M+H]<sup>+</sup>, calculated for C<sub>34</sub>H<sub>37</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>: 543.2818.

### 3.6.4 Synthesis of S18



**S2** (100 mg, 0.27 mmol, 1 eq.) was dissolved in minimum acetic acid (approx. 0.3 mL). The solution was added to **S16** (48 mg, 0.27 mmol, 1 eq.) and the mixture stirred for 30 min. The resulting brown precipitate was filtered off and washed thoroughly with ice-cold methanol to give the pure product as a white solid (51 mg, 0.10 mmol, 36% yield).

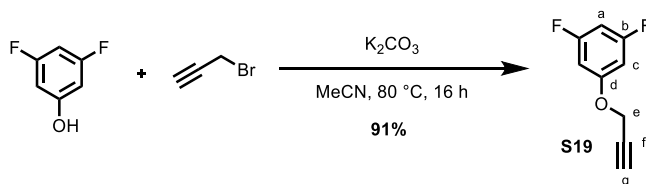
**<sup>1</sup>H NMR** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.78 (br, 1H, H<sub>v</sub> or H<sub>x</sub> or H<sub>y</sub>), 6.90 (s, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.73 (br, 2H, H<sub>i</sub> or H<sub>p</sub>), 6.70 (s, 1H, H<sub>i</sub> or H<sub>p</sub>), 6.65 (br, 1H, H<sub>v</sub> or H<sub>x</sub> or H<sub>y</sub>), 6.35 (br, 1H, H<sub>s</sub>), 6.28 (br, 1H, H<sub>v</sub> or H<sub>x</sub> or H<sub>y</sub>), 4.52 (d, *J* = 2.4 Hz, 2H, H<sub>z</sub>), 4.25 – 4.13 (m, 2H, H<sub>c</sub>), 3.97 – 3.88 (m, 2H, H<sub>d</sub> + H<sub>l</sub>), 3.79 – 3.74 (m, 1H, H<sub>e</sub>), 3.68 – 3.61 (m, 2H, H<sub>d</sub> + H<sub>l</sub>), 2.57 (s, 3H, H<sub>k</sub> or H<sub>h</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.48 (t, *J* = 2.4 Hz, 1H, H<sub>B</sub>), 2.46 – 2.42 (m, 7H, H<sub>a</sub> + H<sub>k</sub> or H<sub>h</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.22 (s, 3H, H<sub>k</sub> or H<sub>h</sub> or H<sub>o</sub> or H<sub>r</sub>), 2.17 (s, 3H, H<sub>k</sub> or H<sub>h</sub> or H<sub>o</sub> or H<sub>r</sub>), 1.82 (s, 3H, H<sub>k</sub> or H<sub>h</sub> or H<sub>o</sub> or H<sub>r</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 162.62 (d, *J* = 247.2 Hz, C<sub>u</sub>), 158.09 (d, *J* = 11.2 Hz, C<sub>w</sub>), 140.36 (br, C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 138.42 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 137.17 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 135.86 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 134.92 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 131.86 (C<sub>f</sub> or C<sub>g</sub> or C<sub>j</sub> or C<sub>m</sub> or C<sub>n</sub> or C<sub>q</sub>), 130.80 (C<sub>i</sub>), 130.54 (br, C<sub>p</sub>), 129.72 (br, C<sub>p</sub>), 129.19 (C<sub>i</sub>), 120.34 (br, C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 110.76 (br, C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 101.25 (br, C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 101.08 (br, C<sub>t</sub> or C<sub>v</sub> or C<sub>x</sub> or C<sub>y</sub>), 80.07 (d, *J* = 1.7 Hz, C<sub>b</sub>), 78.20 (d, *J* = 2.0 Hz, C<sub>B</sub>), 75.83 (d, *J* = 7.9 Hz, C<sub>A</sub>), 74.49 (d, *J* = 7.6 Hz, C<sub>a</sub>), 73.79 (br, C<sub>d</sub>), 72.80 (br, C<sub>s</sub>), 61.67 (br, C<sub>e</sub>), 58.67 – 58.39 (m, C<sub>c</sub>), 56.06 (C<sub>z</sub>), 52.97 (br, C<sub>l</sub>), 20.92 (d, *J* = 2.6 Hz, C<sub>k</sub> or C<sub>h</sub> or C<sub>o</sub> or C<sub>r</sub>), 20.75 (d, *J* = 2.0 Hz, C<sub>k</sub> or C<sub>h</sub> or C<sub>o</sub> or C<sub>r</sub>), 20.33 (q, *J* = 4.3 Hz, C<sub>k</sub> or C<sub>h</sub> or C<sub>o</sub> or C<sub>r</sub>), 19.32 (br, C<sub>k</sub> or C<sub>h</sub> or C<sub>o</sub> or C<sub>r</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -121.20 (s, 1F, F<sub>u</sub>).

**HRMS-ESI(+)**: 525.2902 [M+H]<sup>+</sup>, calculated for C<sub>34</sub>H<sub>38</sub>FN<sub>2</sub>O<sub>2</sub><sup>+</sup>: 525.2912.

### 3.6.5 Synthesis of S19



3,5-difluorophenol (500 mg, 3.85 mmol, 1 eq.) and propargyl bromide (80% in toluene, 0.34 mL, 3.85 mmol, 1 eq.) were dissolved in acetonitrile (19 mL). Potassium carbonate (531 mg, 3.85 mmol, 1 eq.) was added and the mixture stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was washed with water (20 mL) and extracted thoroughly with DCM (4 x 20 mL). The combined organic layers were dried over sodium sulphate, filtered, and condensed to give the crude product as a light yellow liquid that required no further purification (589 mg, 3.50 mmol, 91% yield).

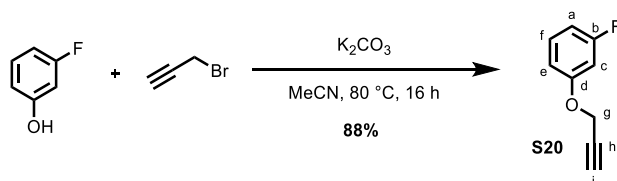
**<sup>1</sup>H NMR** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 6.52 (dd, *J* = 8.8, 2.1 Hz, 2H, H<sub>c</sub>), 6.46 (tt, *J* = 9.1, 2.2 Hz, 1H, H<sub>a</sub>), 4.67 (d, *J* = 2.2 Hz, 2H, H<sub>e</sub>), 2.57 (t, *J* = 2.3 Hz, 1H, H<sub>g</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 163.70 (dd, *J* = 246.7, 15.6 Hz, C<sub>b</sub>), 159.48 (t, *J* = 13.7 Hz, C<sub>d</sub>), 99.31 – 98.62 (m, C<sub>c</sub>), 97.34 (t, *J* = 25.9 Hz, C<sub>a</sub>), 77.60 (d, *J* = 1.5 Hz, C<sub>f</sub>), 76.51 (d, *J* = 6.9 Hz, C<sub>g</sub>), 56.40 (C<sub>e</sub>).

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -108.94 (s, 2F, F<sub>b</sub>).

**HRMS-ESI(+)**: 169.0459 [M+H]<sup>+</sup>, calculated for C<sub>9</sub>H<sub>7</sub>F<sub>2</sub>O<sup>+</sup>: 169.0459.

### 3.6.6 Synthesis of S20



3-fluorophenol (500 mg, 4.46 mmol, 1 eq.) and propargyl bromide (80% in toluene, 0.40 mL, 4.46 mmol, 1 eq.) were dissolved in acetonitrile (22 mL). Potassium carbonate (615 mg, 4.46 mmol, 1 eq.) was added and the mixture stirred at 80 °C for 16 h. After cooling to room temperature, the mixture was washed with water (20 mL) and extracted thoroughly with DCM (4 x 20 mL). The combined organic layers were dried over sodium sulphate, filtered, and condensed to give the crude product as a light yellow liquid that required no further purification (589 mg, 3.92 mmol, 88% yield).

**<sup>1</sup>H NMR** (<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 7.32 – 7.27 (m, 1H, H<sub>i</sub>), 6.83 – 6.78 (m, 1H, H<sub>e</sub>), 6.78 – 6.72 (m, 2H, H<sub>a</sub> + H<sub>c</sub>), 4.72 (d, *J* = 2.4 Hz, 2H, H<sub>g</sub>), 2.58 (t, *J* = 2.4 Hz, 1H, H<sub>i</sub>).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ = 163.64 (d, *J* = 245.5 Hz, C<sub>b</sub>), 158.95 (d, *J* = 10.9 Hz, C<sub>d</sub>), 130.39 (d, *J* = 9.9 Hz, C<sub>f</sub>), 110.73 (d, *J* = 3.3 Hz, C<sub>e</sub>), 108.56 (d, *J* = 21.2 Hz, C<sub>a</sub>), 102.94 (dd, *J* = 25.1, 2.8 Hz, C<sub>c</sub>), 78.18 (d, *J* = 2.0 Hz, C<sub>h</sub>), 76.03 (d, *J* = 8.2 Hz, C<sub>i</sub>), 56.15 (C<sub>g</sub>).

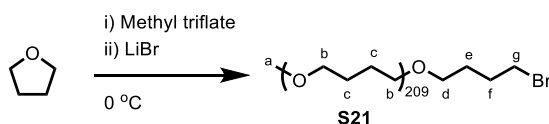
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ = -111.38 (s, 1F, F<sub>b</sub>).

**HRMS-ESI(+)**: 151.0554 [M+H]<sup>+</sup>, calculated for C<sub>9</sub>H<sub>8</sub>FO<sup>+</sup>: 151.0554.

## 4 Synthesis of PTHF and incorporation of mechanophores and reference compounds

### 4.1 Synthesis of PTHF

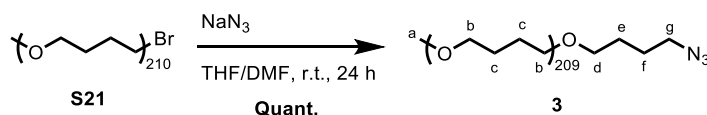
#### 4.1.1 Synthesis of S21



In an oven-dried round-bottom flask was added dry THF (100 mL, 1.23 mol, 1500 eq.). The solution was placed under nitrogen before methyl triflate (0.090 mL, 0.820 mmol, 1 eq.) was added. The mixture was cooled in an ice-water bath and stirring was adjusted throughout the reaction to maintain proper mixing of the solution as it became more viscous. Termination of the polymerisation was carried out after 5 h by adding a solution of lithium bromide (2.14 g, 24.6 mmol, 30 eq.) in minimal dry THF. Stirring was carried out for a further 30 min after addition of the terminating agent. The polymer was precipitated in water (700 mL). The water was decanted and the polymer collected before being dissolved in DCM. The solution was thoroughly washed with brine before being dried over sodium sulfate and condensed. The crude polymer was dissolved in minimum diethyl ether and the solution stored overnight at -22 °C allowing the polymer to precipitate after which it could be collected by filtration to yield a white fluffy solid (12.2 g,  $M_n$  = 15 kDa as determined by  $^1\text{H}$  NMR,  $M_n$  = 47 kDa as determined by GPC, PDI = 1.12 as determined by GPC).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 3.60 – 3.16 (br,  $\text{H}_b$ ,  $\text{H}_d$ ,  $\text{H}_g$ ), 3.31 (s,  $\text{H}_a$ ), 1.93 (p,  $J$  = 7.0 Hz,  $\text{H}_f$ ), 1.78 – 1.44 (br,  $\text{H}_c$ ,  $\text{H}_e$ ).

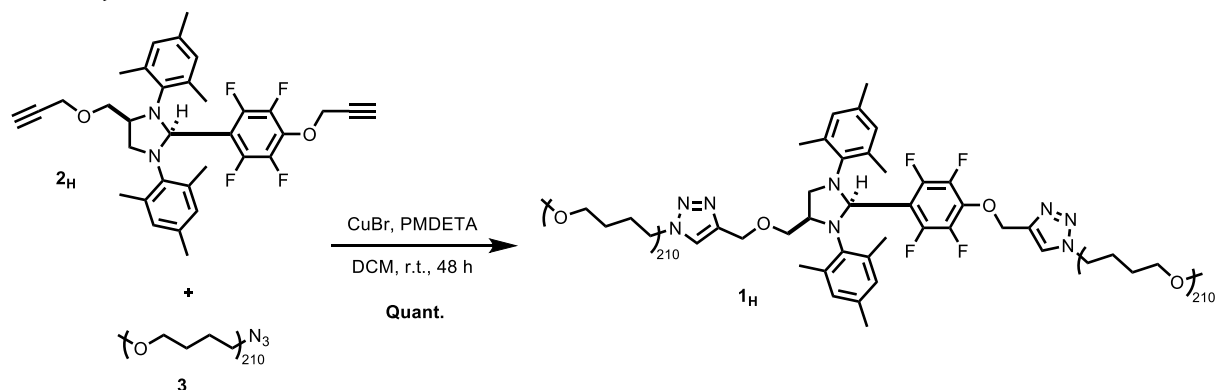
#### 4.1.2 Synthesis of 3



S21 (12.0 g, 0.789 mmol, 1 eq.) was dissolved in THF (300 mL) and DMF (100 mL). Sodium azide was added (1.46 g, 22.5 mmol, 30 eq.) and the mixture stirred at room temperature for 24 h. The solution was condensed to remove THF leaving a viscous slurry of polymer and DMF. The polymer was precipitated in water (700 mL). The water was decanted and the polymer collected before being dissolved in DCM. The solution was thoroughly washed with brine before being dried over sodium sulfate and condensed. The crude polymer was dissolved in minimum diethyl ether and the solution stored at -22 °C until the polymer precipitated at which point it could be collected by filtration to yield a white fluffy solid (11.3 g,  $M_n$  = 47 kDa as determined by GPC, PDI = 1.12).

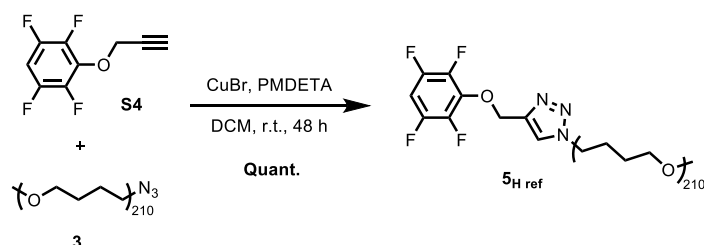
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  = 3.60 – 3.16 (br,  $\text{H}_b$ ,  $\text{H}_d$ ), 3.31 (s,  $\text{H}_a$ ), 3.28 (t,  $J$  = 6.5 Hz,  $\text{H}_g$ ), 1.78 – 1.44 (br,  $\text{H}_c$ ,  $\text{H}_e$ ,  $\text{H}_f$ ).

## 4.2 Synthesis of 1<sub>H</sub>



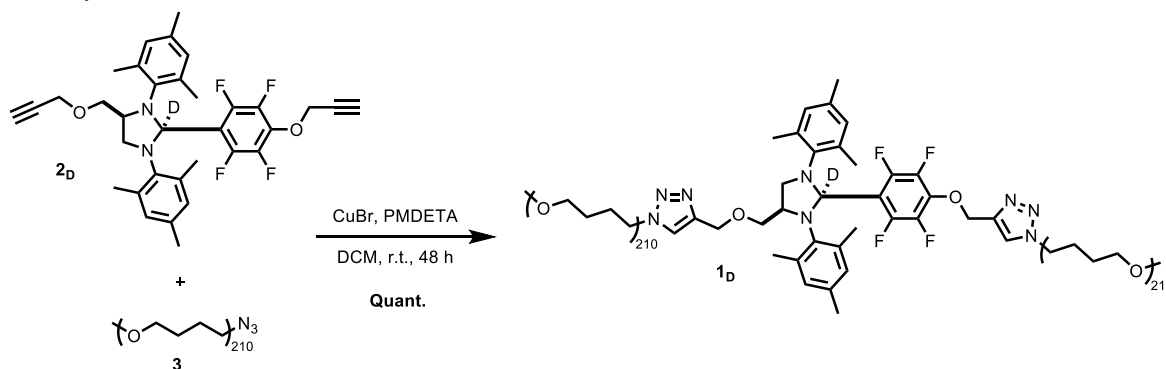
**3** (480 mg, 32  $\mu\text{mol}$ , 2.5 eq.) and **2<sub>H</sub>** (7 mg, 12  $\mu\text{mol}$ , 1.0 eq.) were dissolved in DCM (20 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (3 mL) and PMDETA (23  $\mu\text{L}$ , 110  $\mu\text{mol}$ , 9.0 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (10 mg, 72  $\mu\text{mol}$ , 6.0 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

## 4.3 Synthesis of 5<sub>H ref</sub>



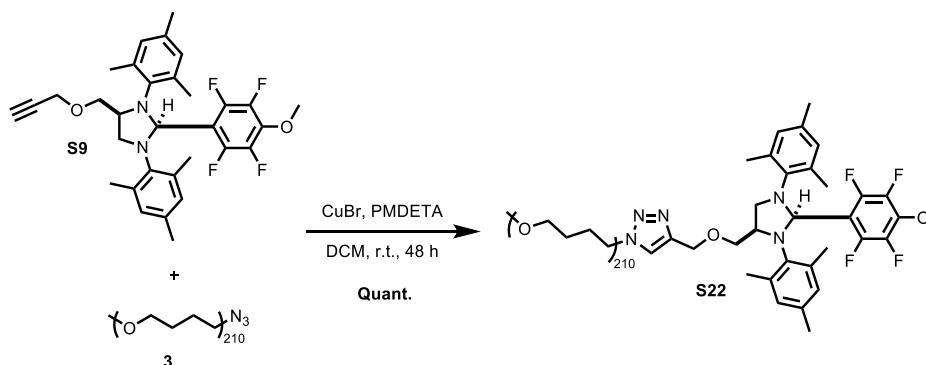
**3** (120 mg, 8  $\mu\text{mol}$ , 1.25 eq.) and **S4** (1 mg, 6  $\mu\text{mol}$ , 1.00 eq.) were dissolved in DCM (5 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (2 mL) and PMDETA (6  $\mu\text{L}$ , 27  $\mu\text{mol}$ , 4.50 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (3 mg, 18  $\mu\text{mol}$ , 3.00 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

#### 4.4 Synthesis of 1<sub>D</sub>



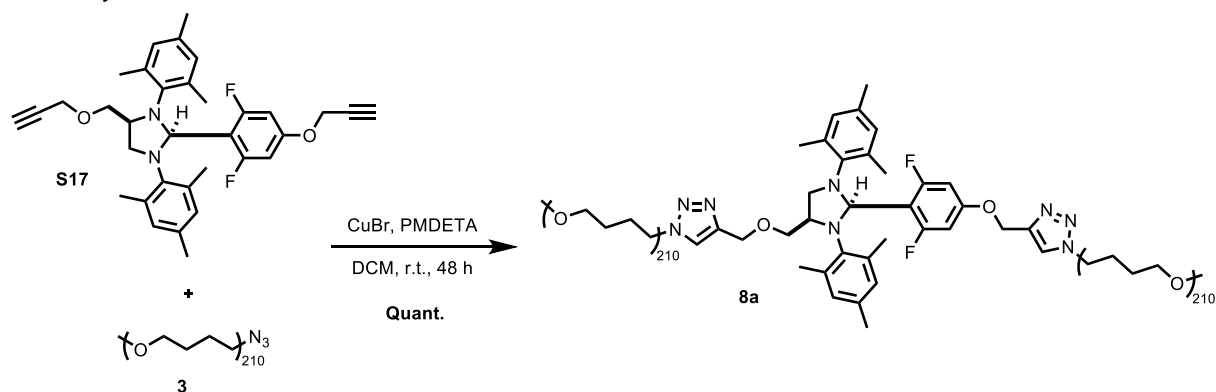
**3** (480 mg, 32  $\mu\text{mol}$ , 2.5 eq.) and **2<sub>D</sub>** (7 mg, 12  $\mu\text{mol}$ , 1.0 eq.) were dissolved in DCM (20 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (3 mL) and PMDETA (23  $\mu\text{L}$ , 110  $\mu\text{mol}$ , 9.0 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (10 mg, 72  $\mu\text{mol}$ , 6.0 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

#### 4.5 Synthesis of S22



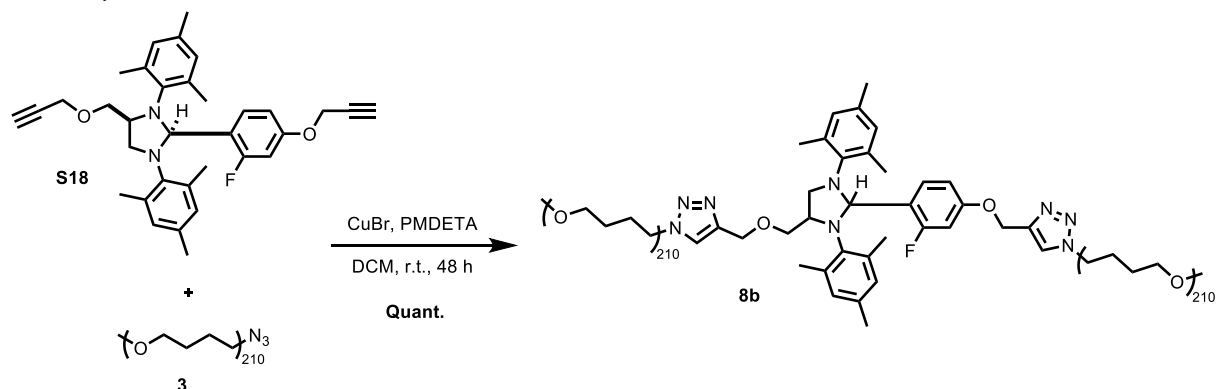
**3** (120 mg, 8  $\mu\text{mol}$ , 1.25 eq.) and **S9** (3 mg, 6  $\mu\text{mol}$ , 1 eq.) were dissolved in DCM (5 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (2 mL) and PMDETA (6  $\mu\text{L}$ , 27  $\mu\text{mol}$ , 4.5 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (3 mg, 18  $\mu\text{mol}$ , 3 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

#### 4.6 Synthesis of 8a



**3** (240 mg, 16  $\mu\text{mol}$ , 2.5 eq.) and **S17** (3.5 mg, 6  $\mu\text{mol}$ , 1.0 eq.) were dissolved in DCM (20 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (1 mL) and PMDETA (23  $\mu\text{L}$ , 110  $\mu\text{mol}$ , 18.0 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (10 mg, 72  $\mu\text{mol}$ , 12.0 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

#### 4.7 Synthesis of 8b

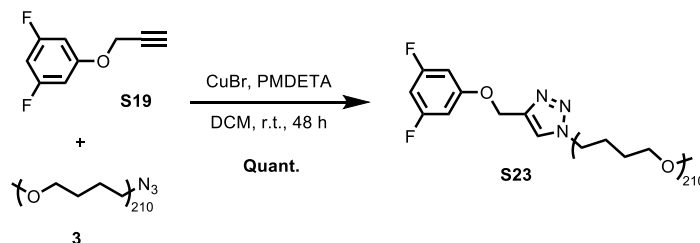


**3** (240 mg, 16  $\mu\text{mol}$ , 2.5 eq.) and **S18** (3.5 mg, 6  $\mu\text{mol}$ , 1.0 eq.) were dissolved in DCM (20 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (1 mL) and PMDETA (23  $\mu\text{L}$ , 110  $\mu\text{mol}$ , 18.0 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (10 mg, 72  $\mu\text{mol}$ , 12.0 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried



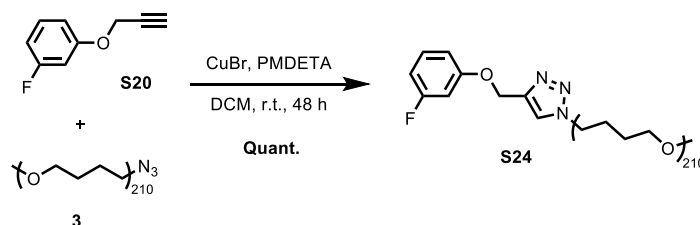
over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

#### 4.8 Synthesis of S23



**3** (120 mg, 8  $\mu$ mol, 1.25 eq.) and **S19** (1 mg, 6  $\mu$ mol, 1.00 eq.) were dissolved in DCM (5 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (1 mL) and PMDETA (6  $\mu$ L, 27  $\mu$ mol, 4.50 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (3 mg, 18  $\mu$ mol, 3.00 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

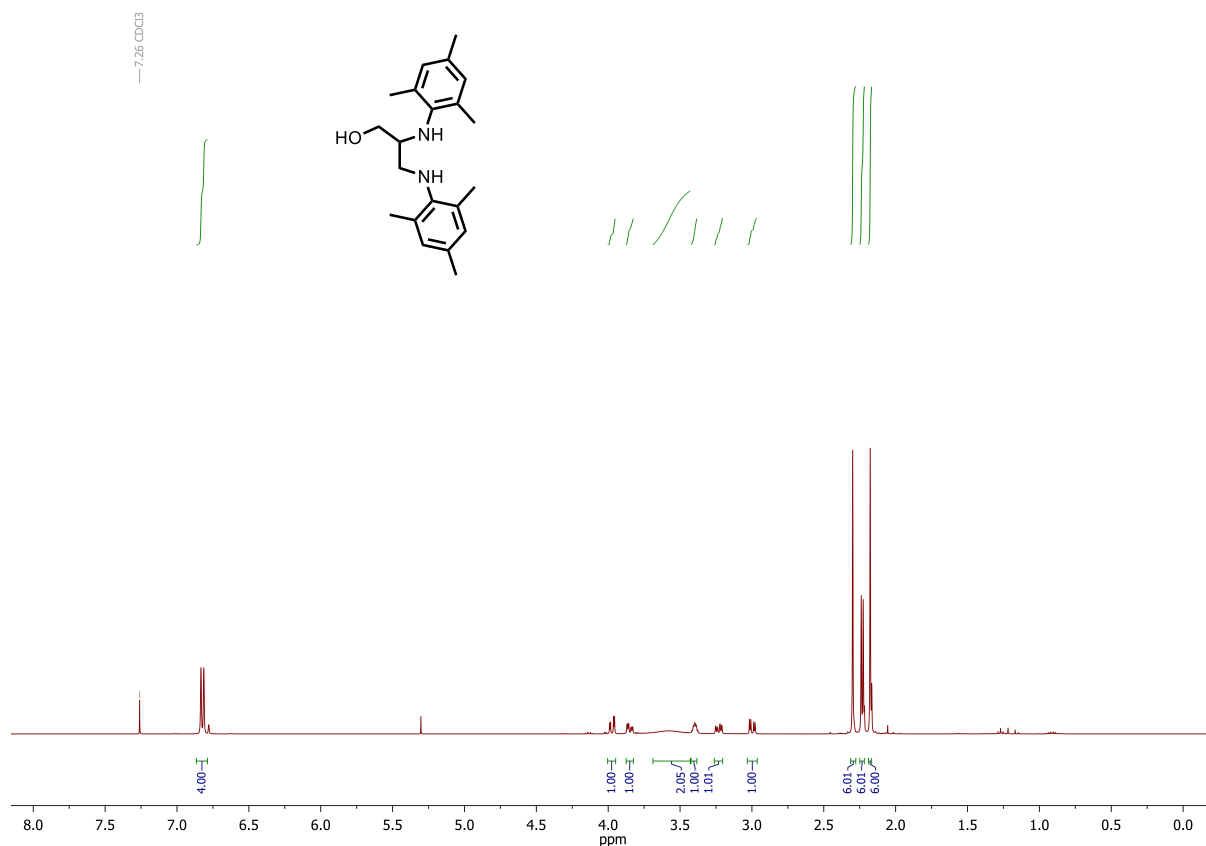
#### 4.9 Synthesis of S24



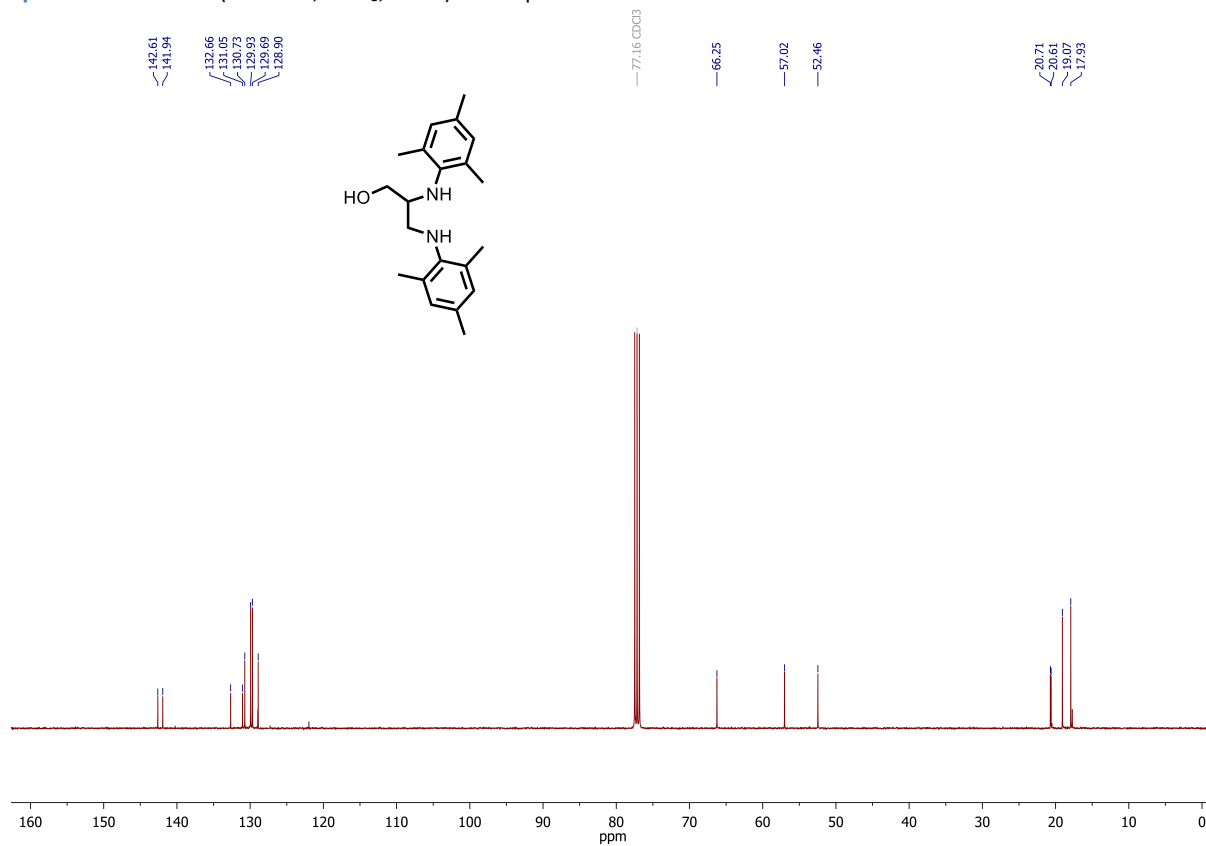
**3** (106 mg, 7  $\mu$ mol, 1.4 eq.) and **S20** (1 mg, 5  $\mu$ mol, 1.00 eq.) were dissolved in DCM (5 mL) and added to a sealed microwave vial. The solution was degassed via three freeze-thaw-pump cycles. In a separate sealed microwave vial was added DCM (1 mL) and PMDETA (6  $\mu$ L, 27  $\mu$ mol, 5.40 eq.). This solution was also degassed via three freeze-thaw-pump cycles before being transferred via cannula onto copper(I) bromide (3 mg, 18  $\mu$ mol, 3.60 eq.) in a third sealed microwave vial. This mixture was stirred until all of the copper(I) bromide had dissolved before the solution was degassed via a single freeze-thaw-pump cycle. This solution was then transferred via cannula onto the reaction mixture in the first microwave vial. The mixture was stirred for 48 h. The mixture was washed thoroughly with aqueous EDTA solution (0.25 M, pH 7) to remove copper species before being dried over sodium sulfate and condensed to give the product polymer which was thoroughly dried under high vacuum. Once dried, the polymer can be carefully washed with acetonitrile to remove impurities before being dried under high vacuum again.

## 5 NMR Spectra

### 5.1 Spectra of S1

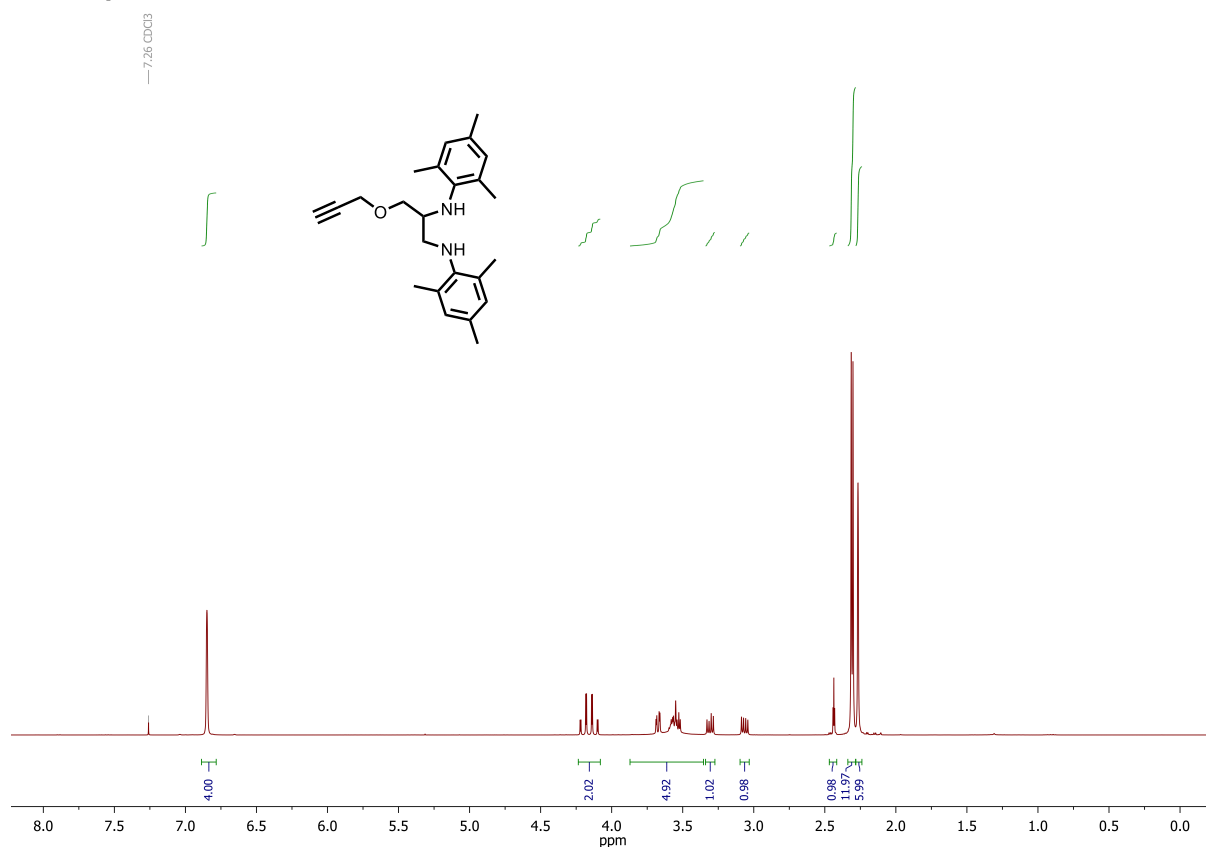


**Spectrum 1.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound S1.

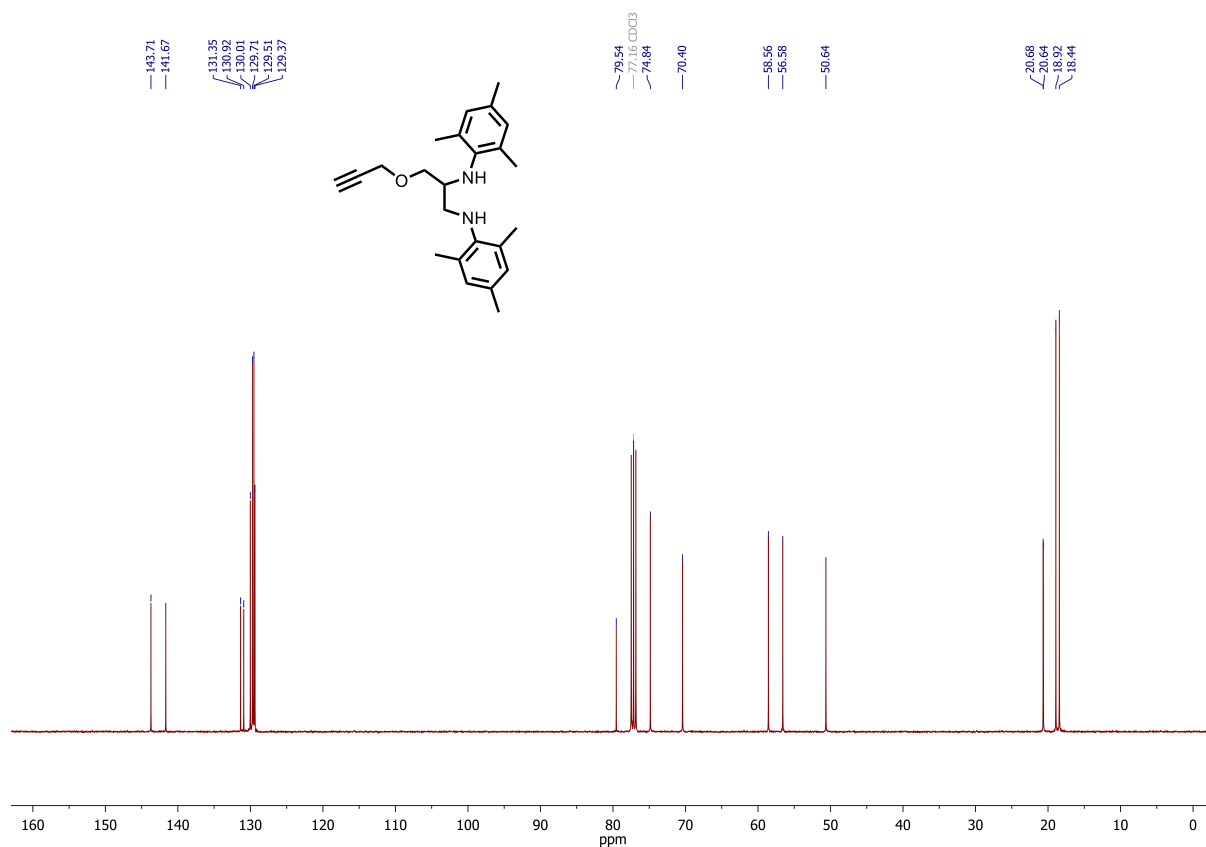


**Spectrum 2.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K) of compound S1.

## 5.2 Spectra of S2

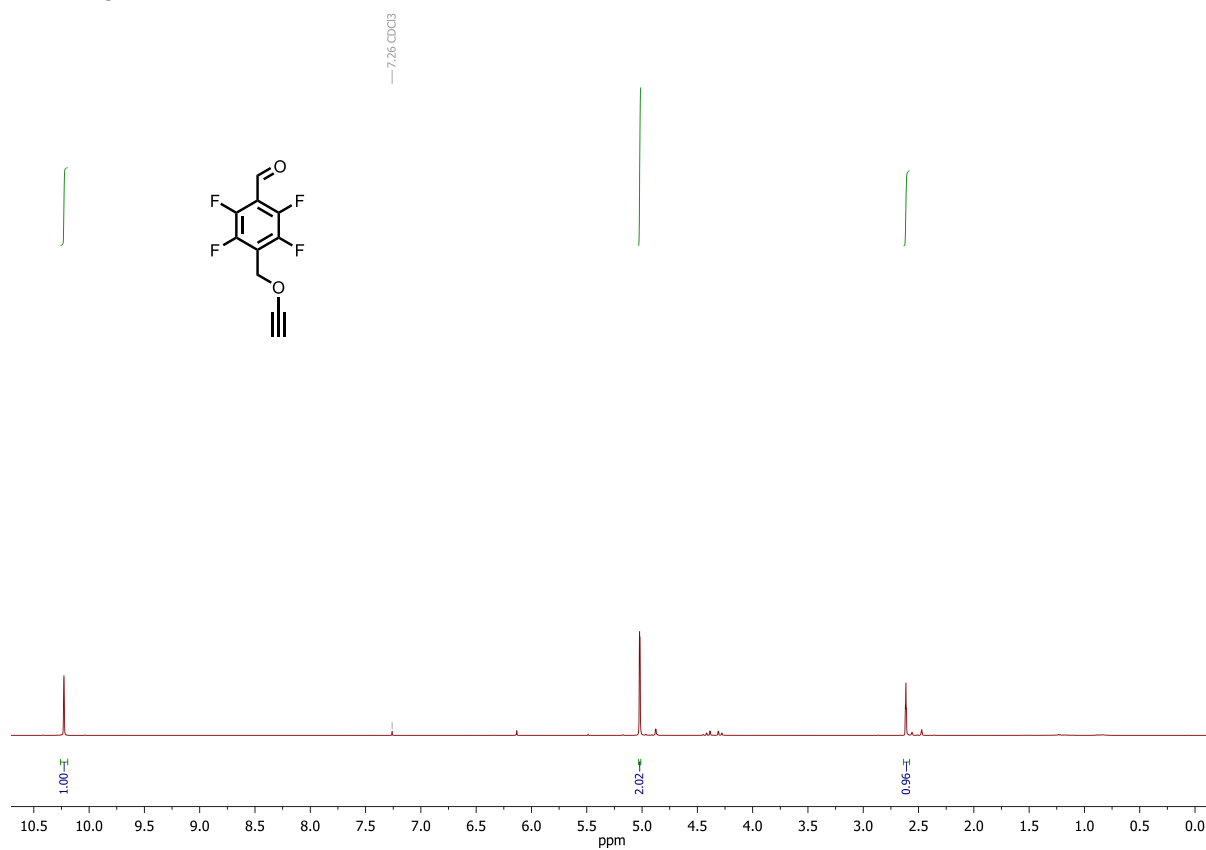


**Spectrum 3.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound **S2**.

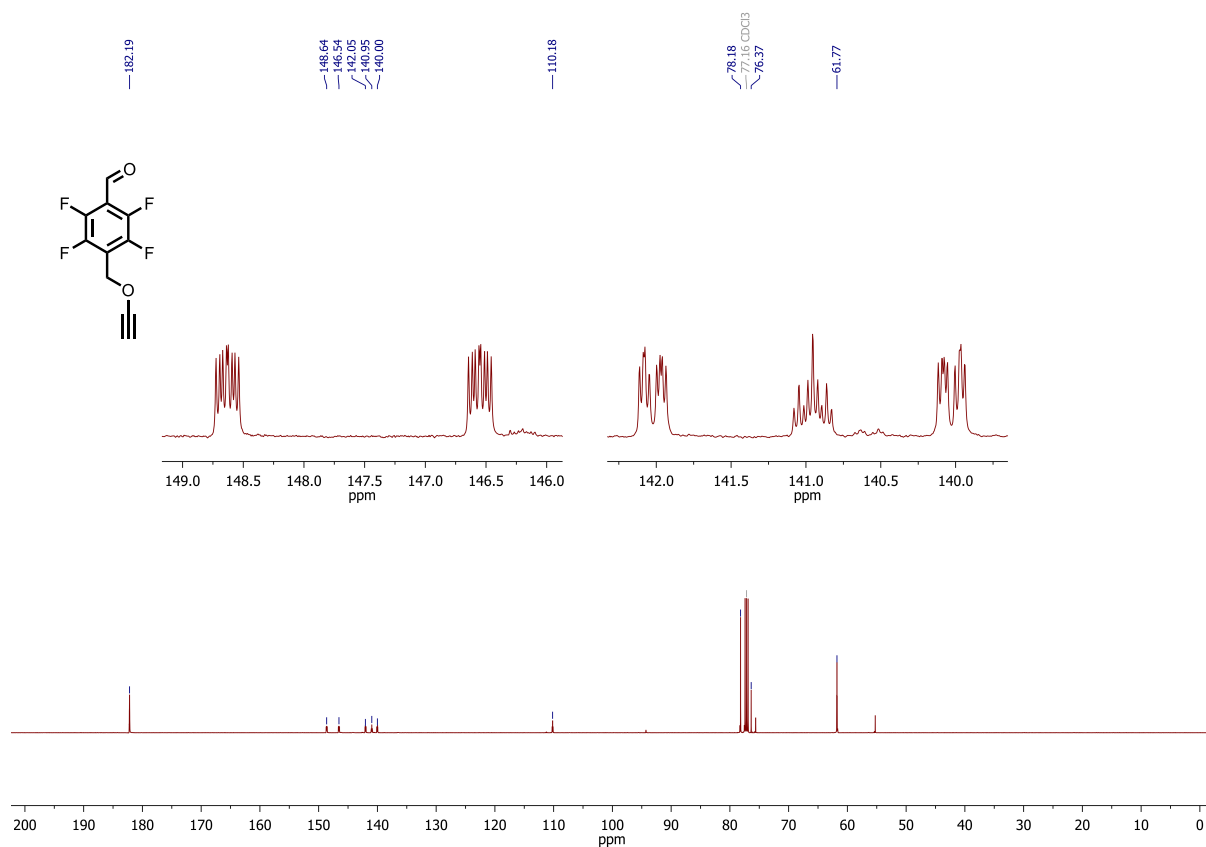


**Spectrum 4.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K) of compound **S2**.

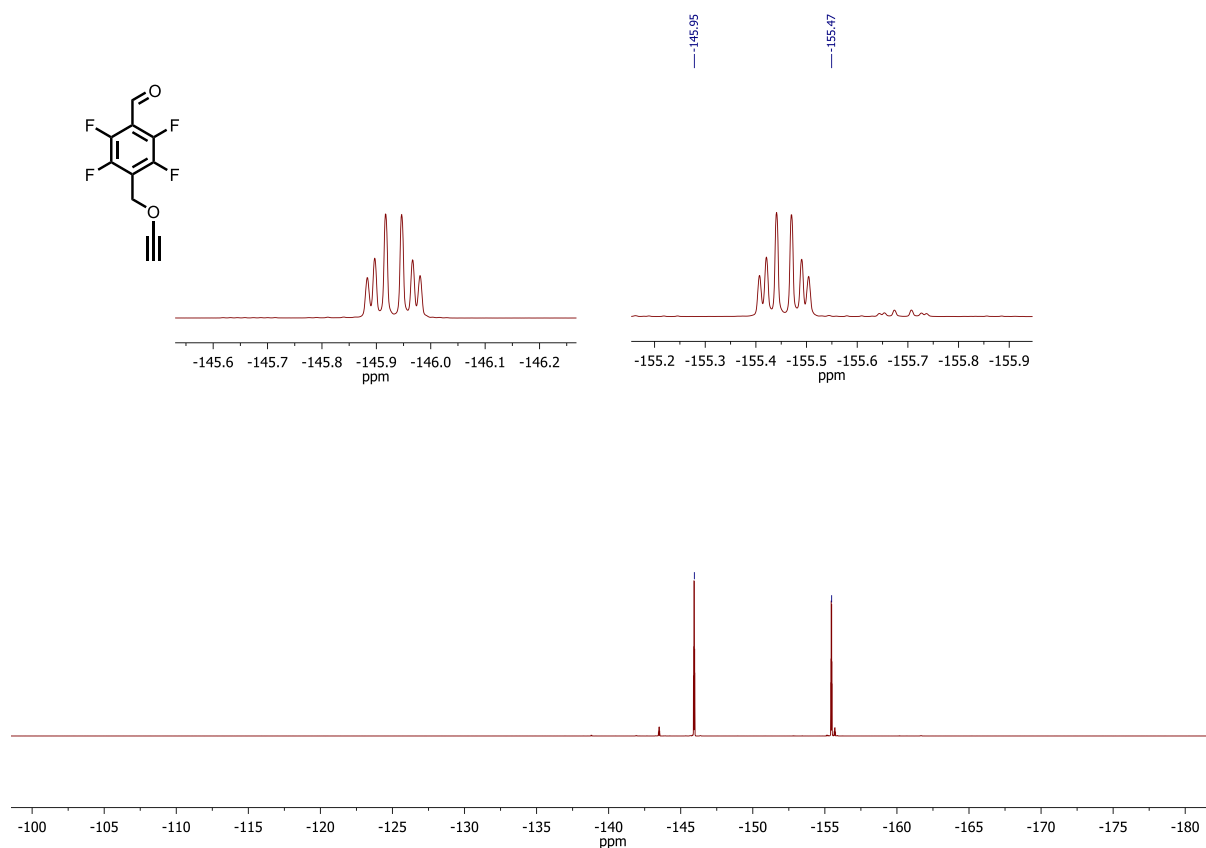
### 5.3 Spectra of S3



**Spectrum 5.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **S3**.

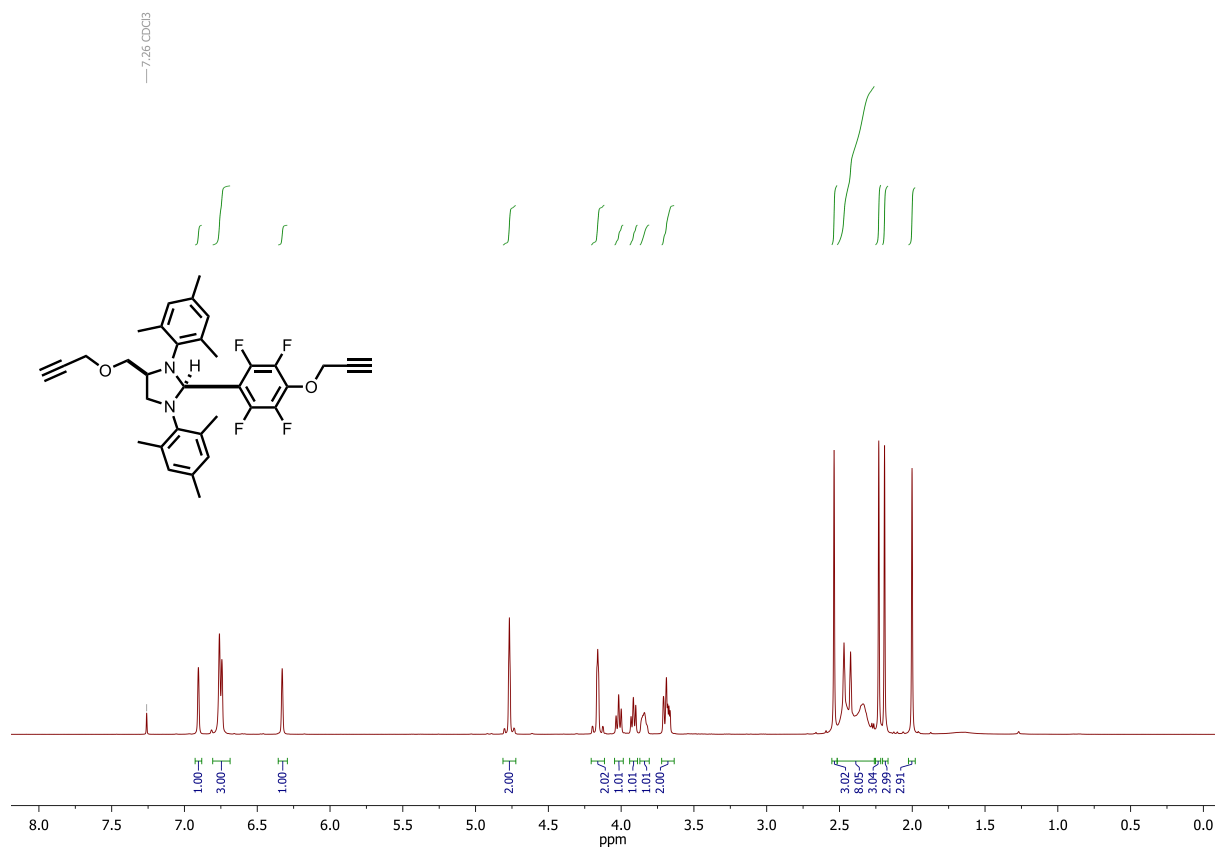


**Spectrum 6.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S3**.

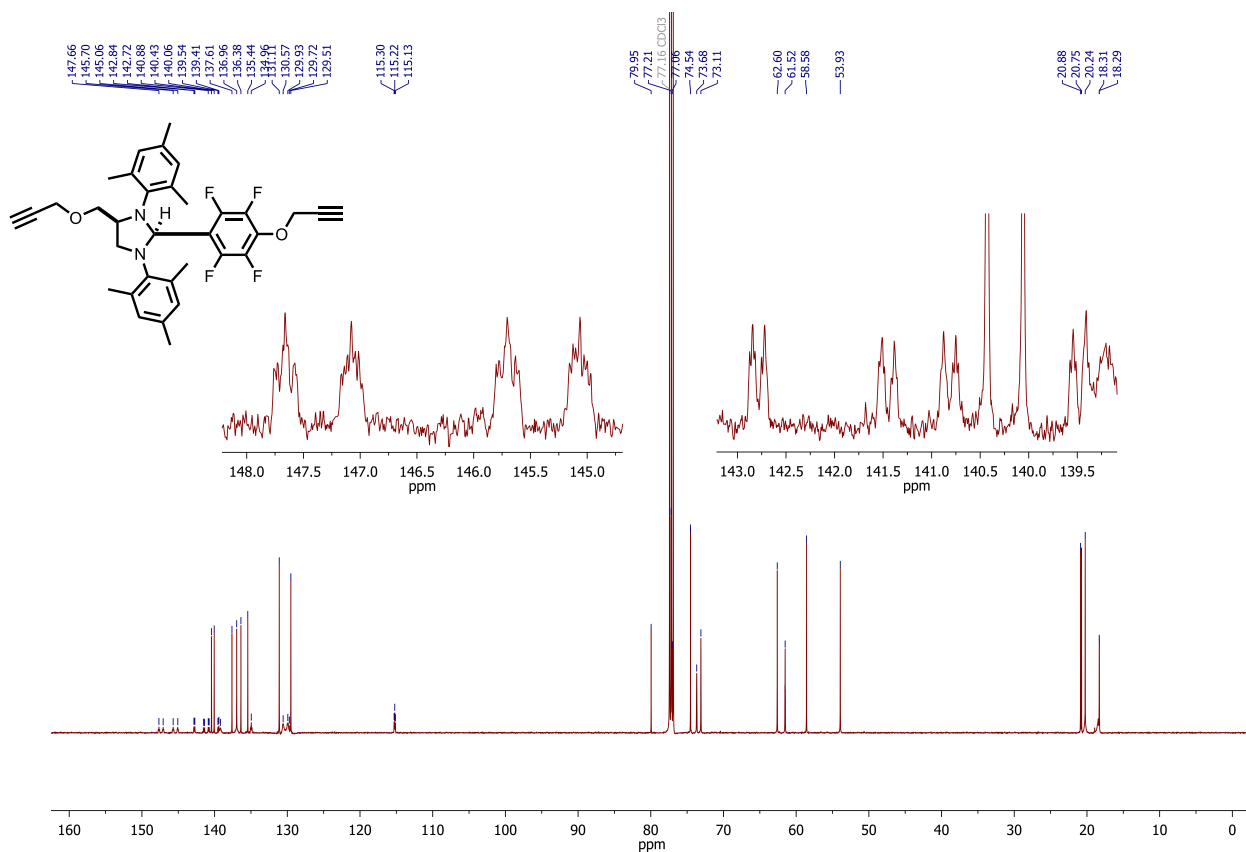


**Spectrum 7.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **53**.

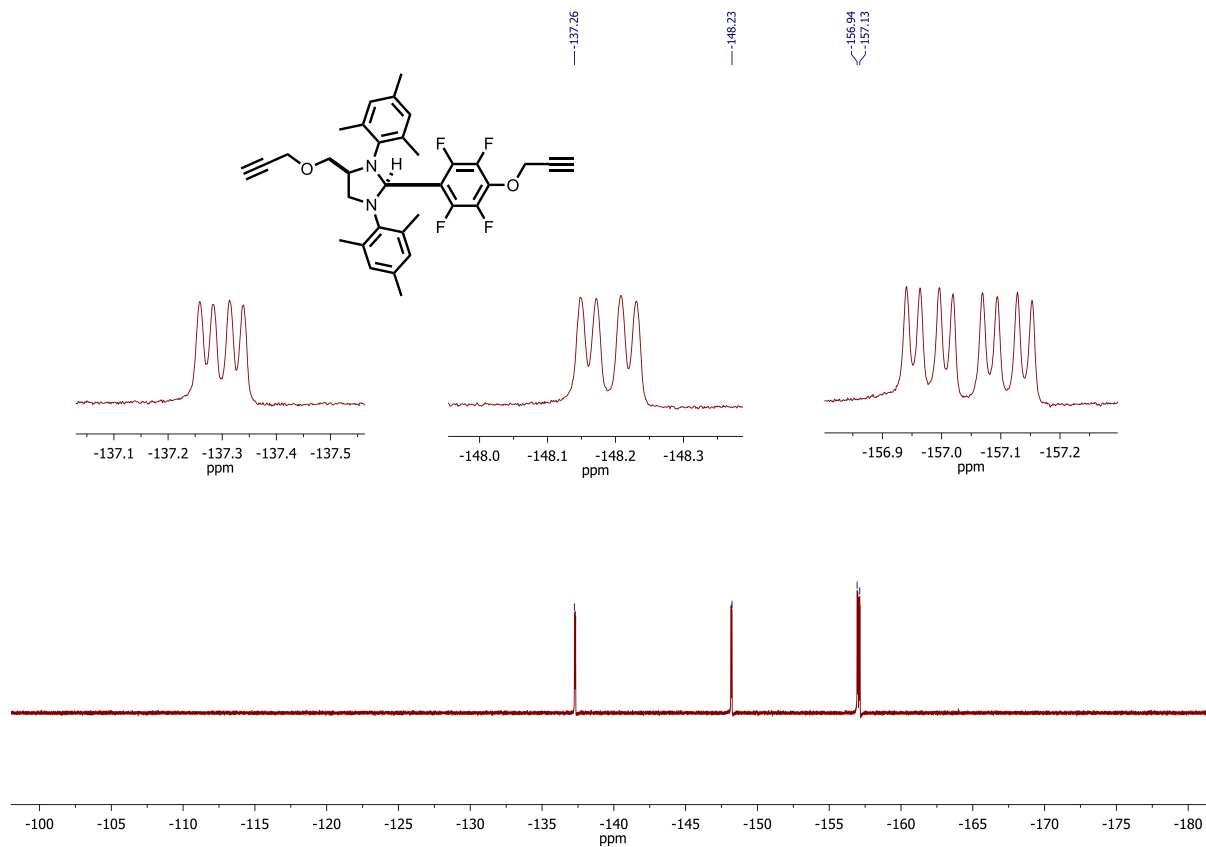
## 5.4 Spectra of **2<sub>H</sub>**



**Spectrum 8.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **2<sub>H</sub>**.

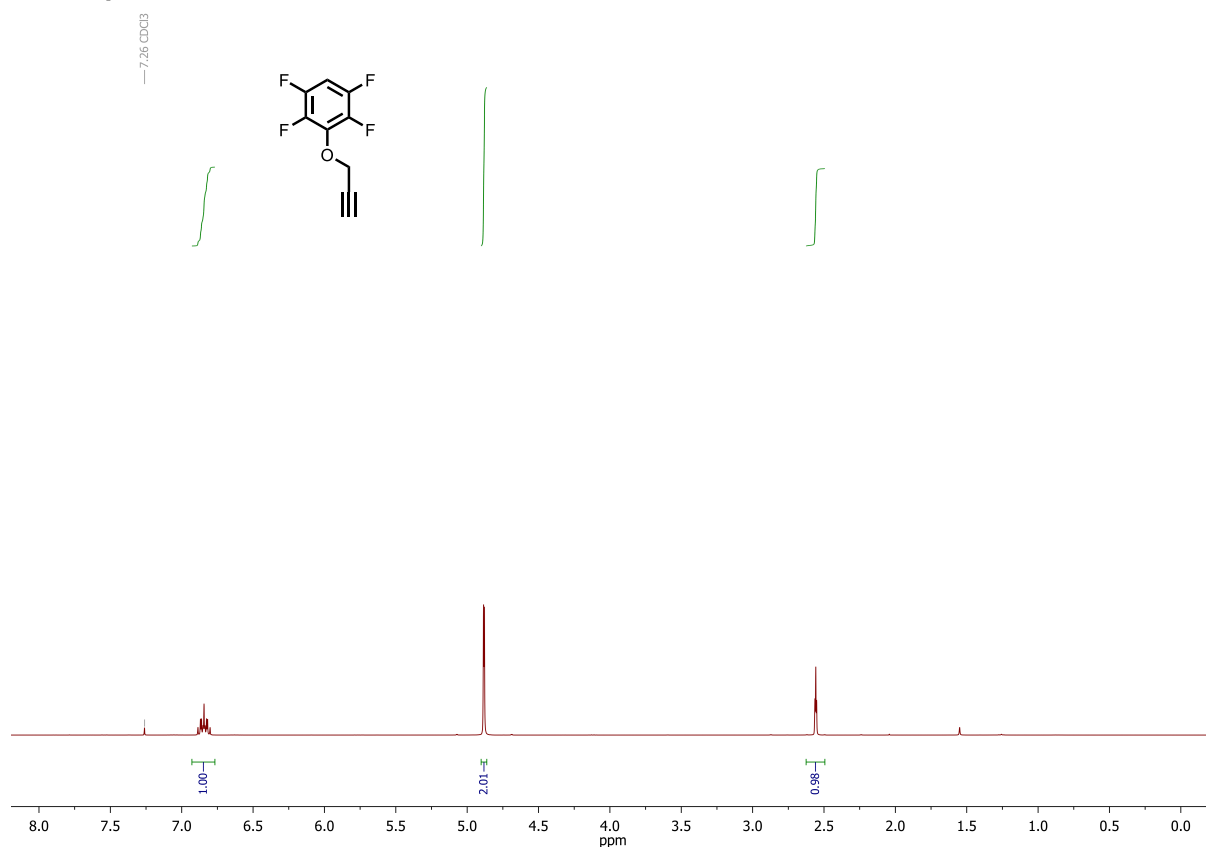


**Spectrum 9.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **2H**.

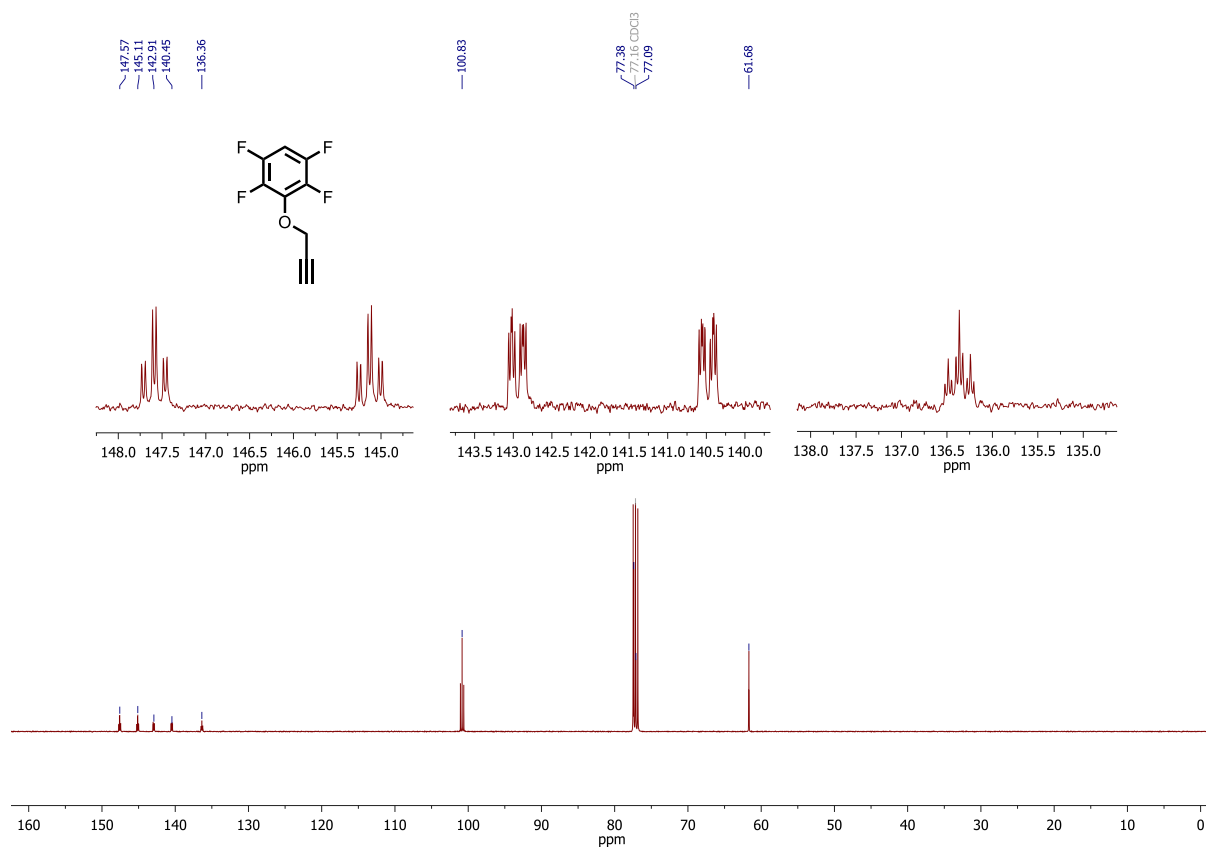


**Spectrum 10.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **2H**.

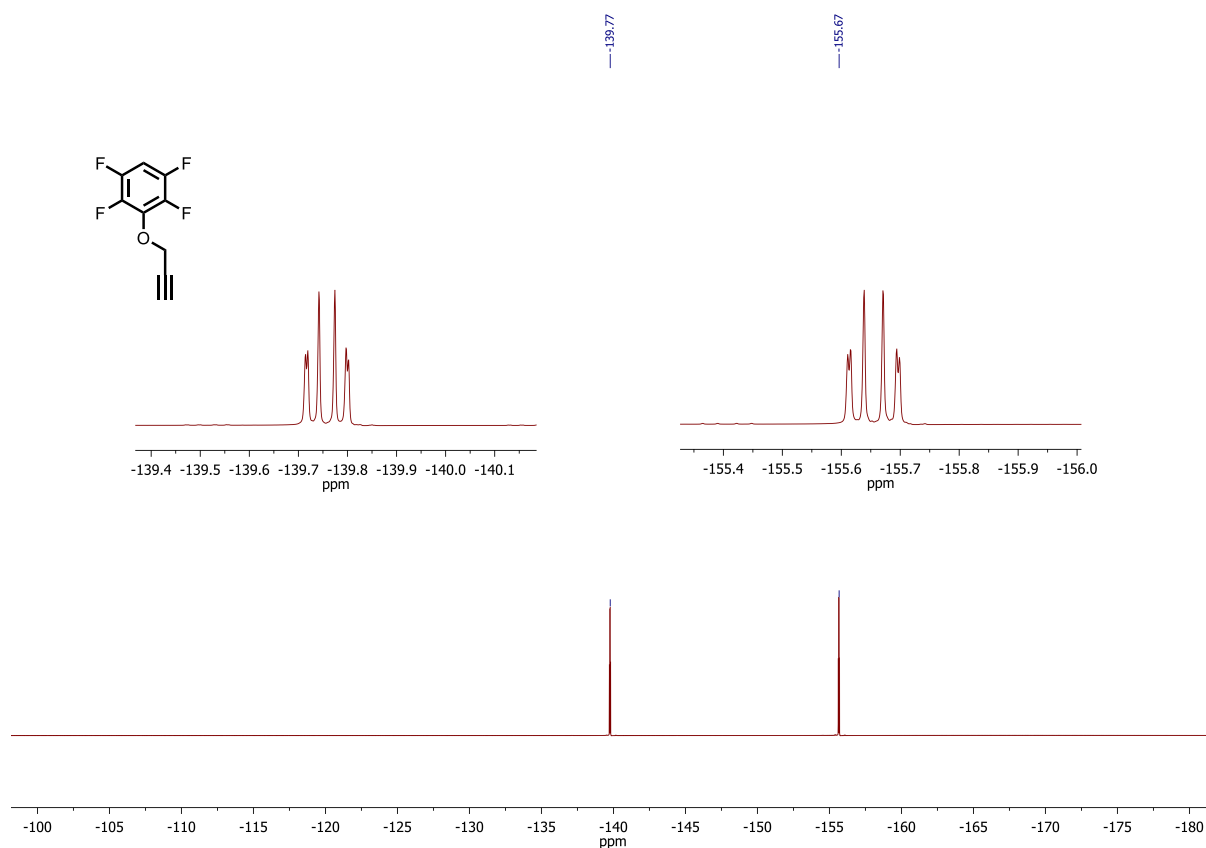
## 5.5 Spectra of S4



**Spectrum 11.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S4**.

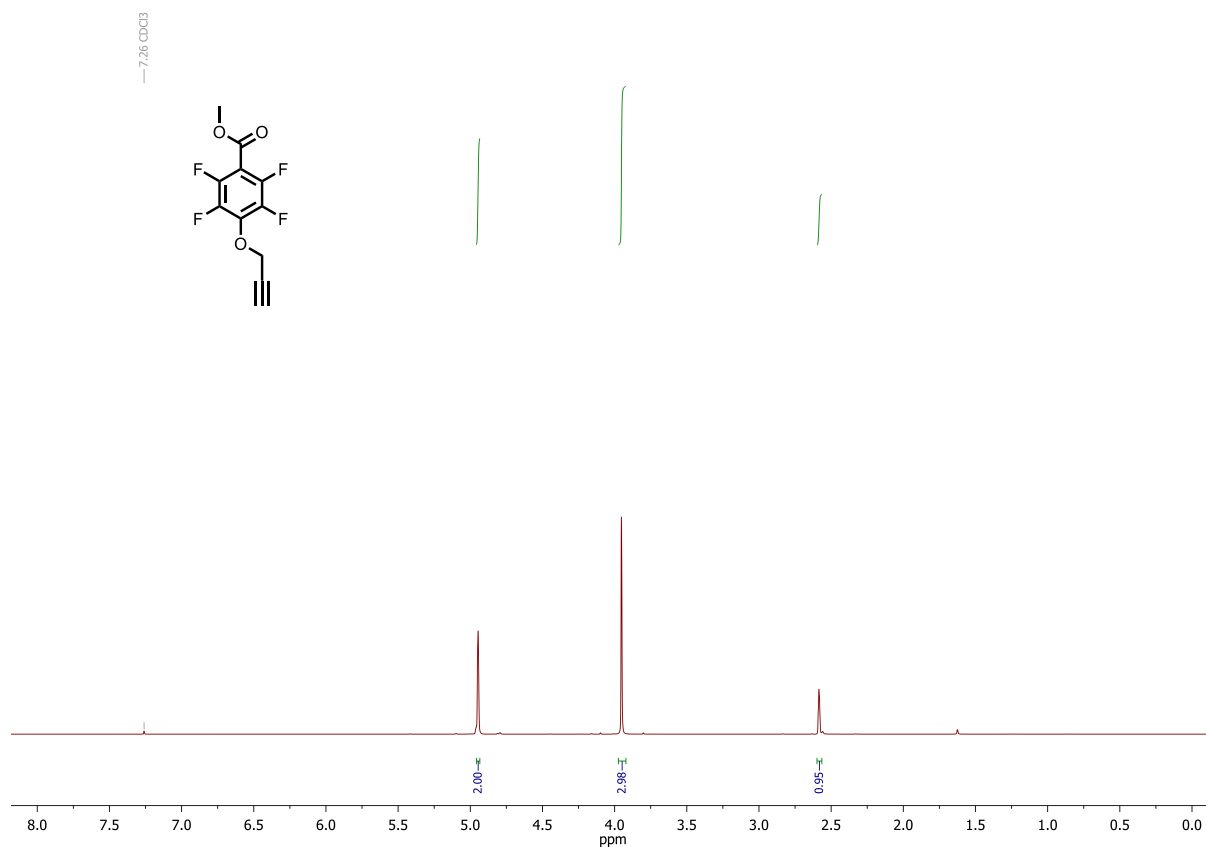


**Spectrum 12.**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S4**.



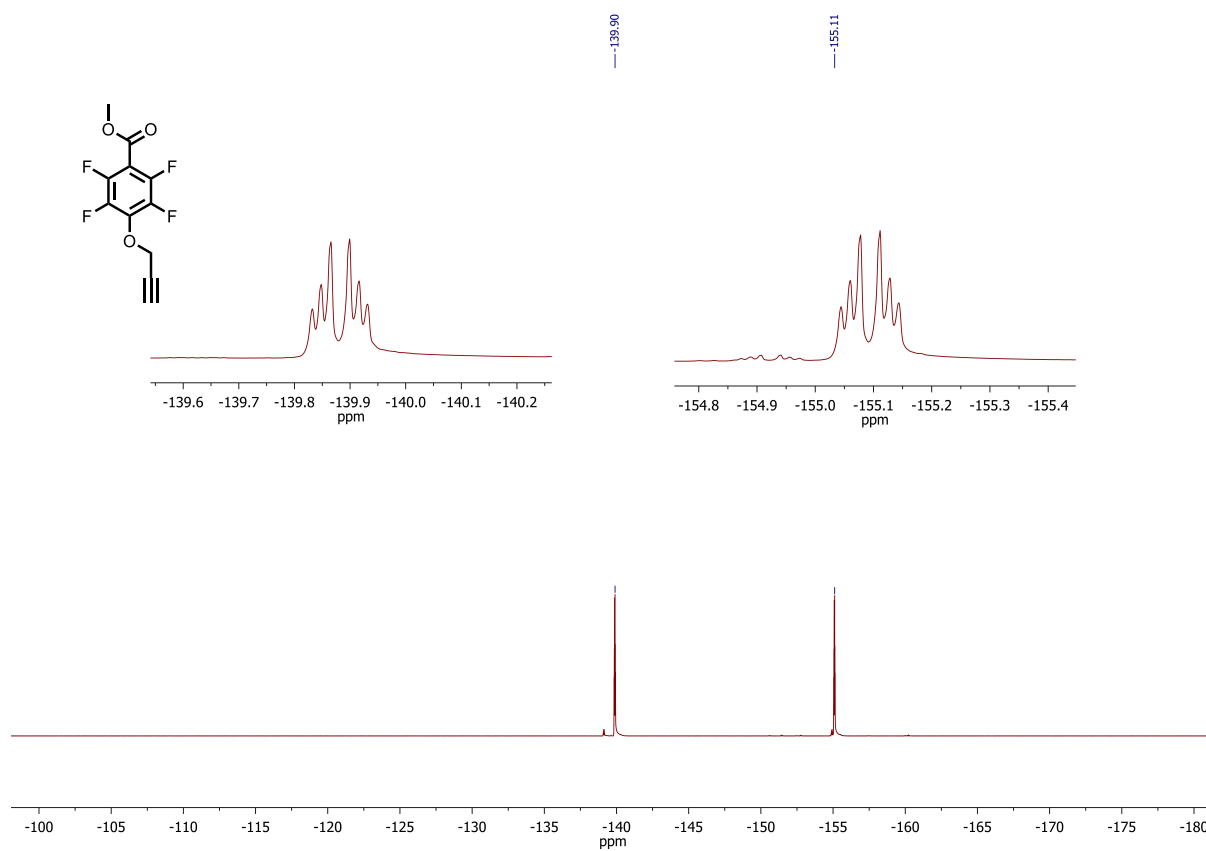
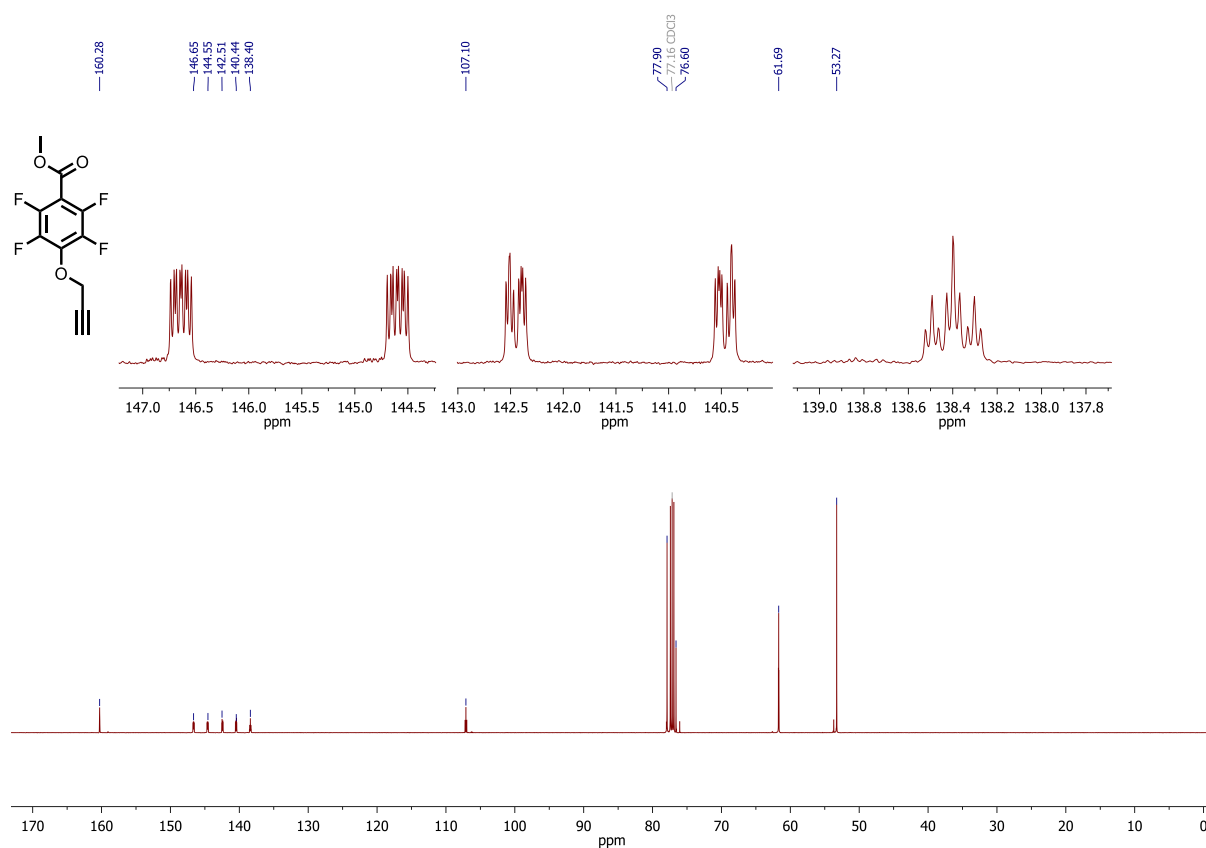
**Spectrum 13.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **S4**.

## 5.6 Spectra of S5

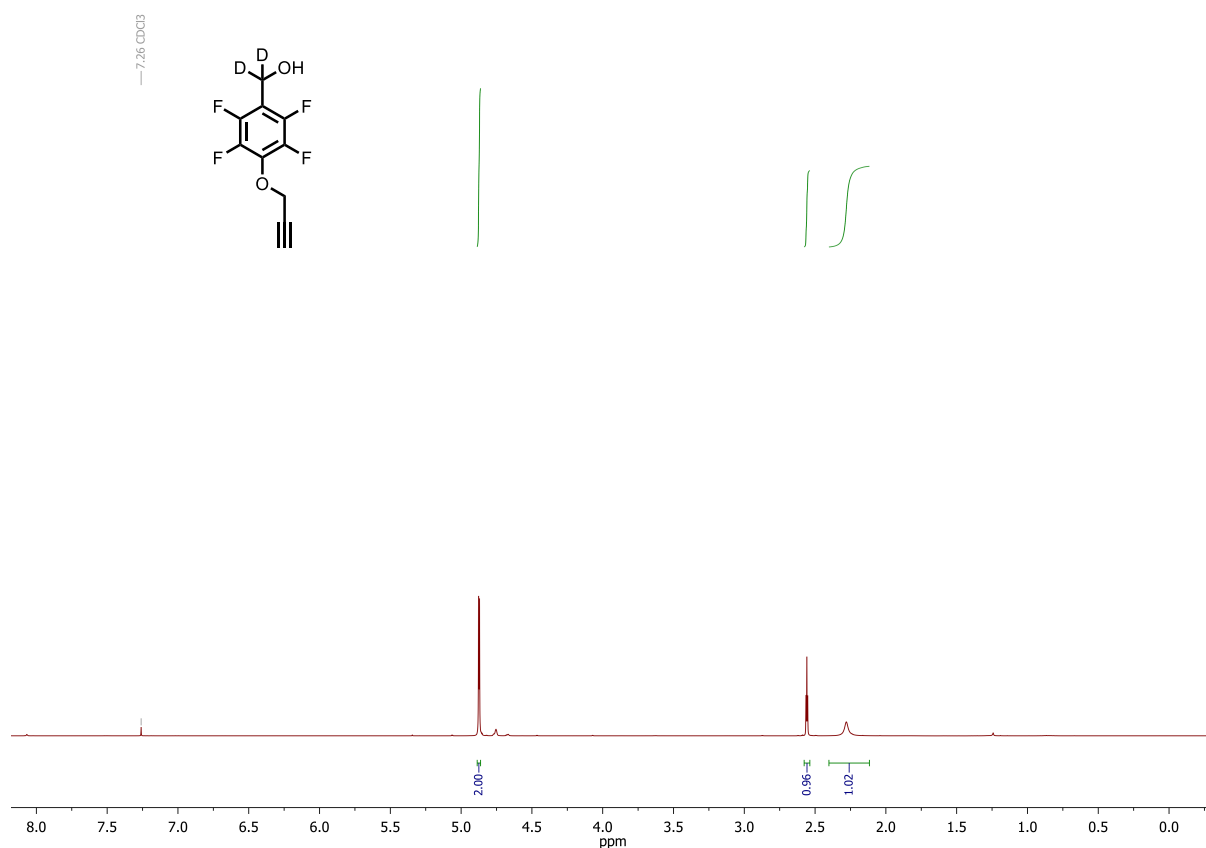


**Spectrum 14.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **S5**.

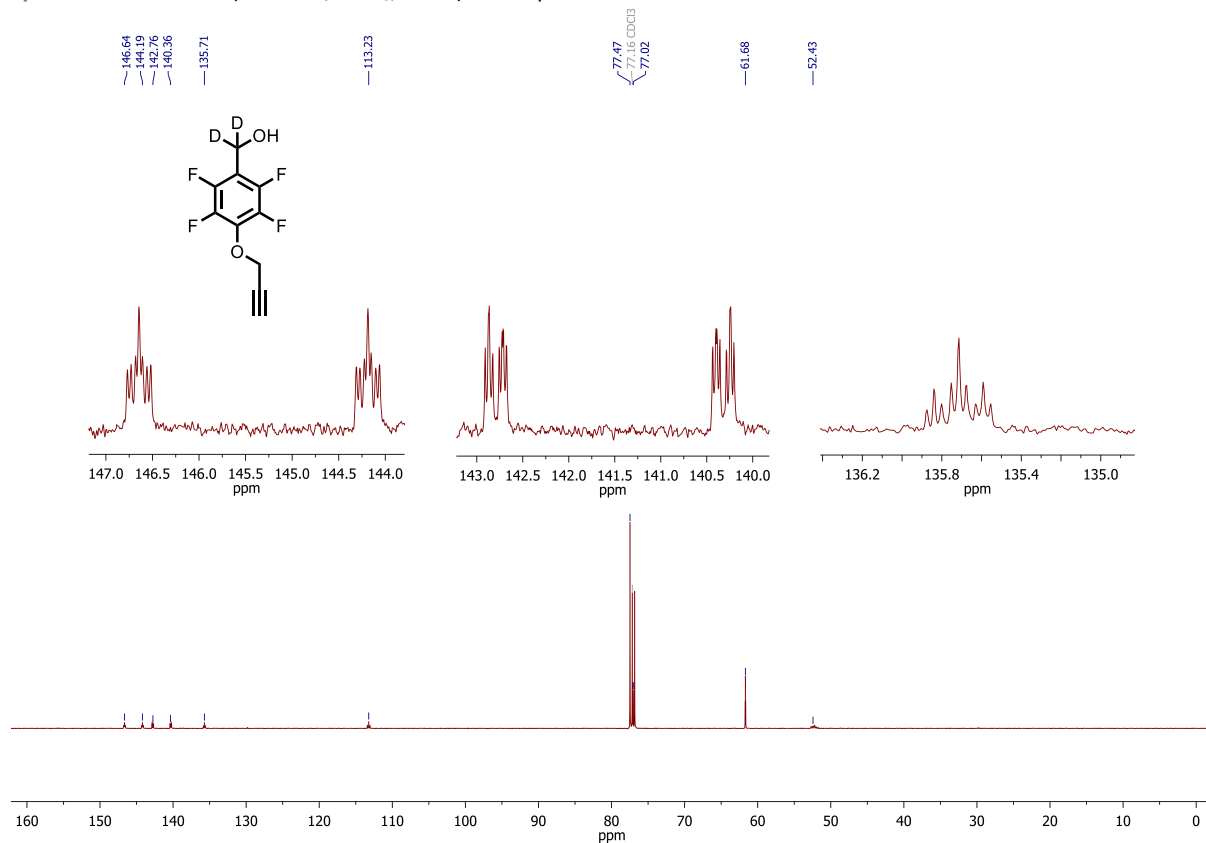




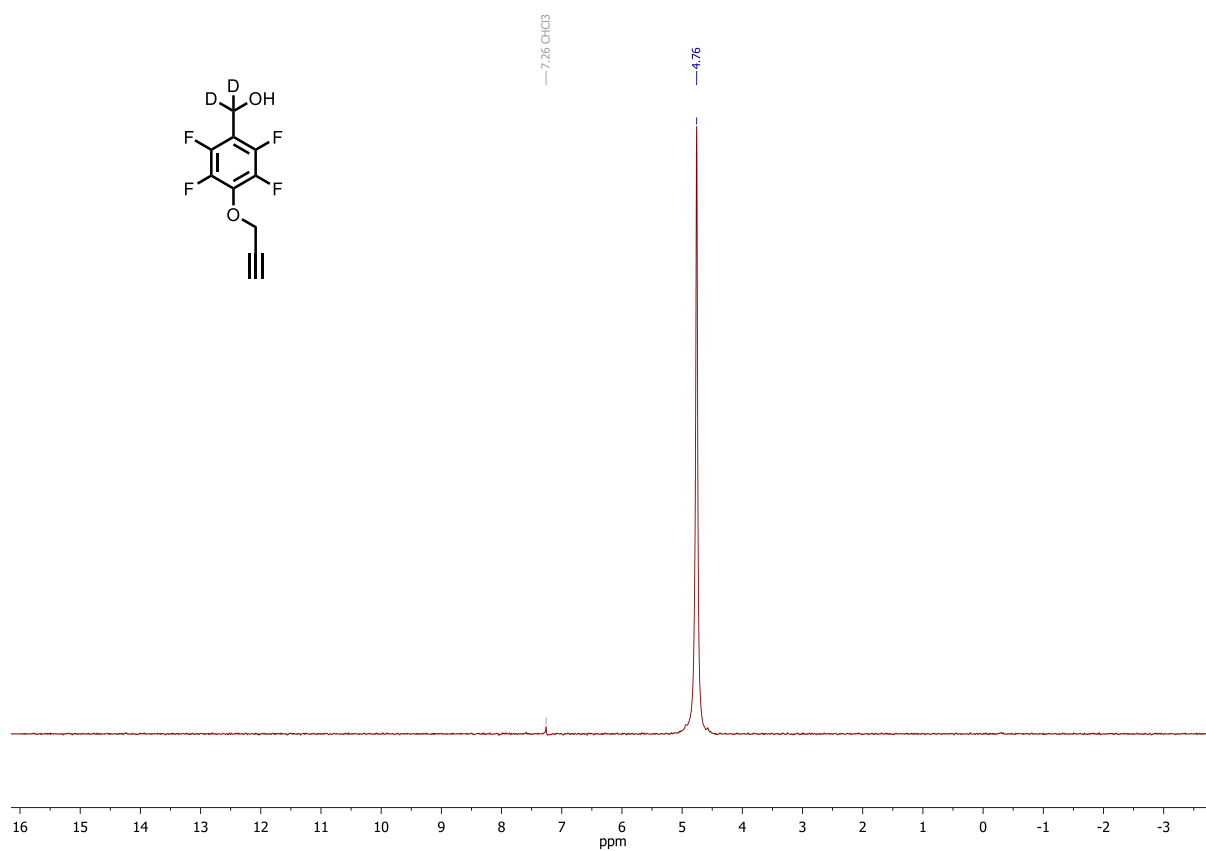
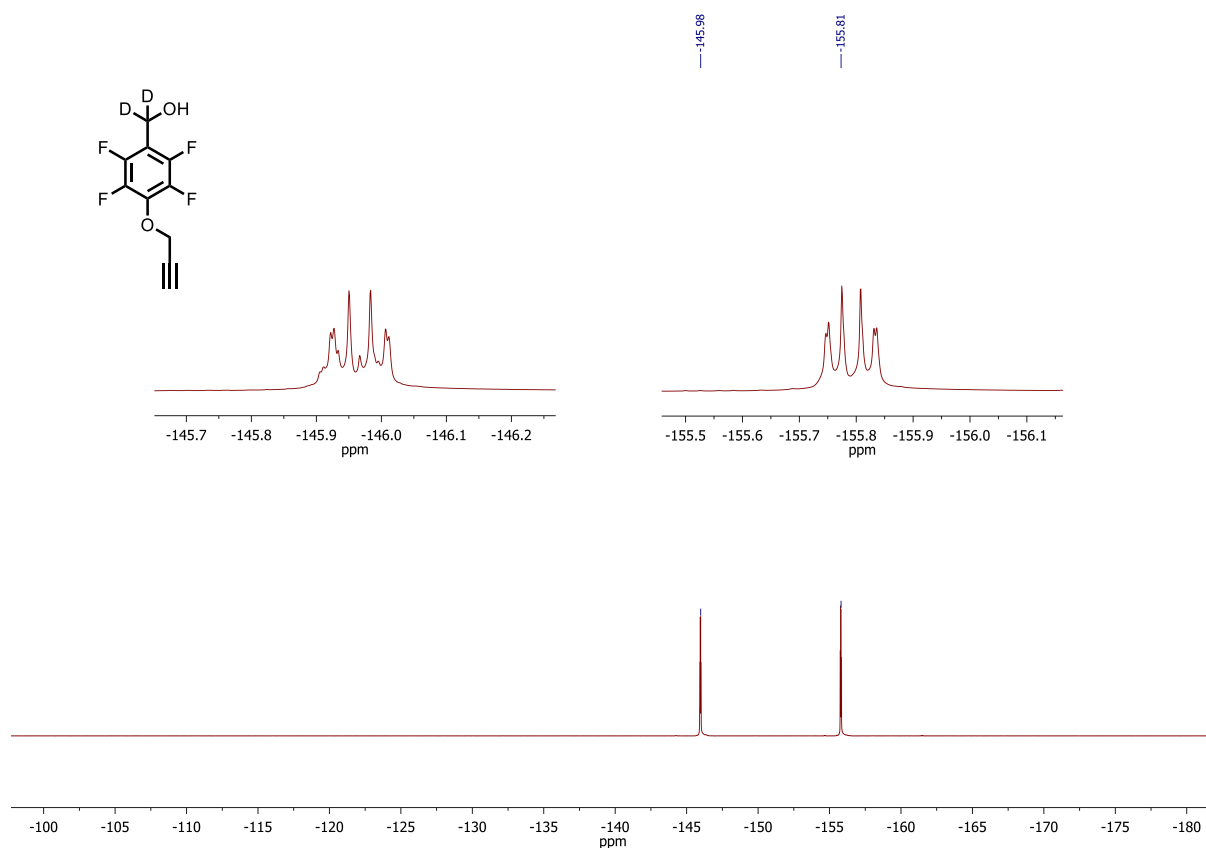
## 5.7 Spectra of S6



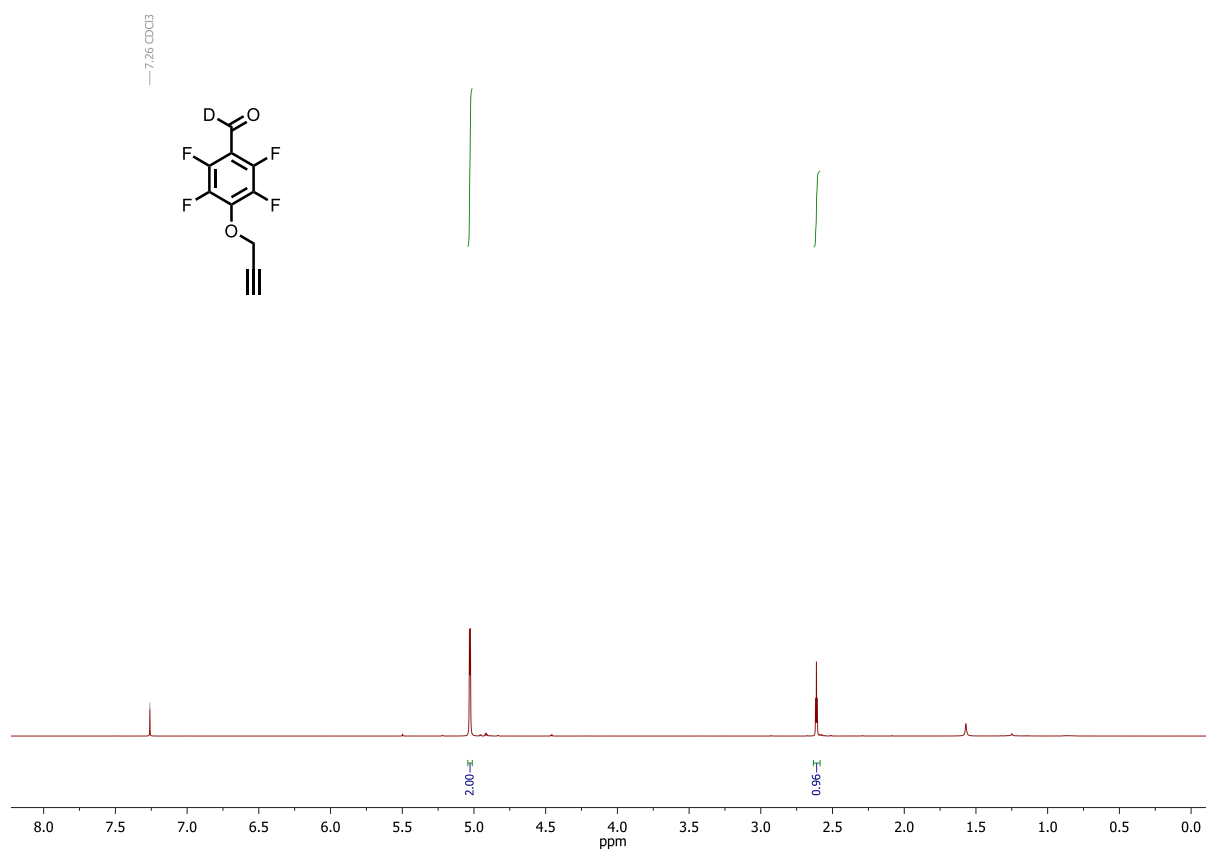
**Spectrum 17.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound **S6**.



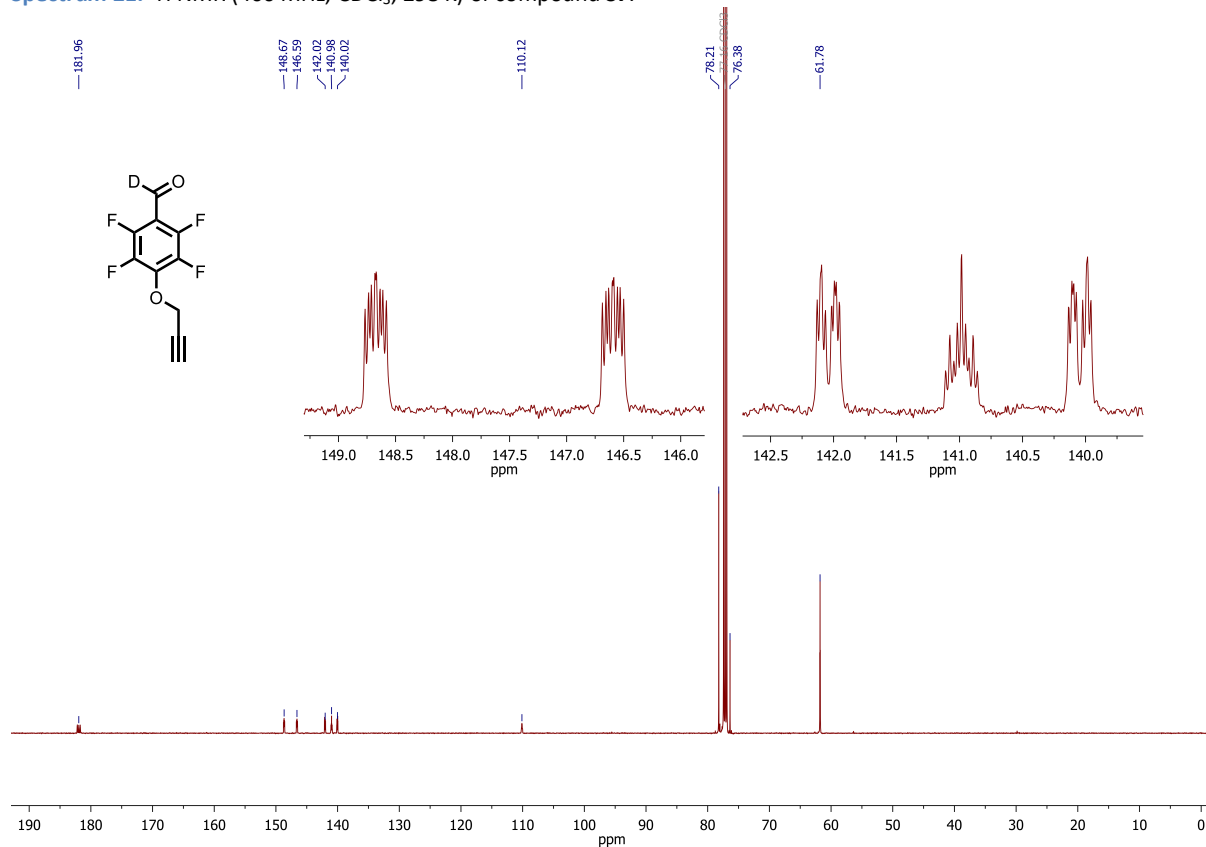
**Spectrum 18.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K) of compound **S6**.



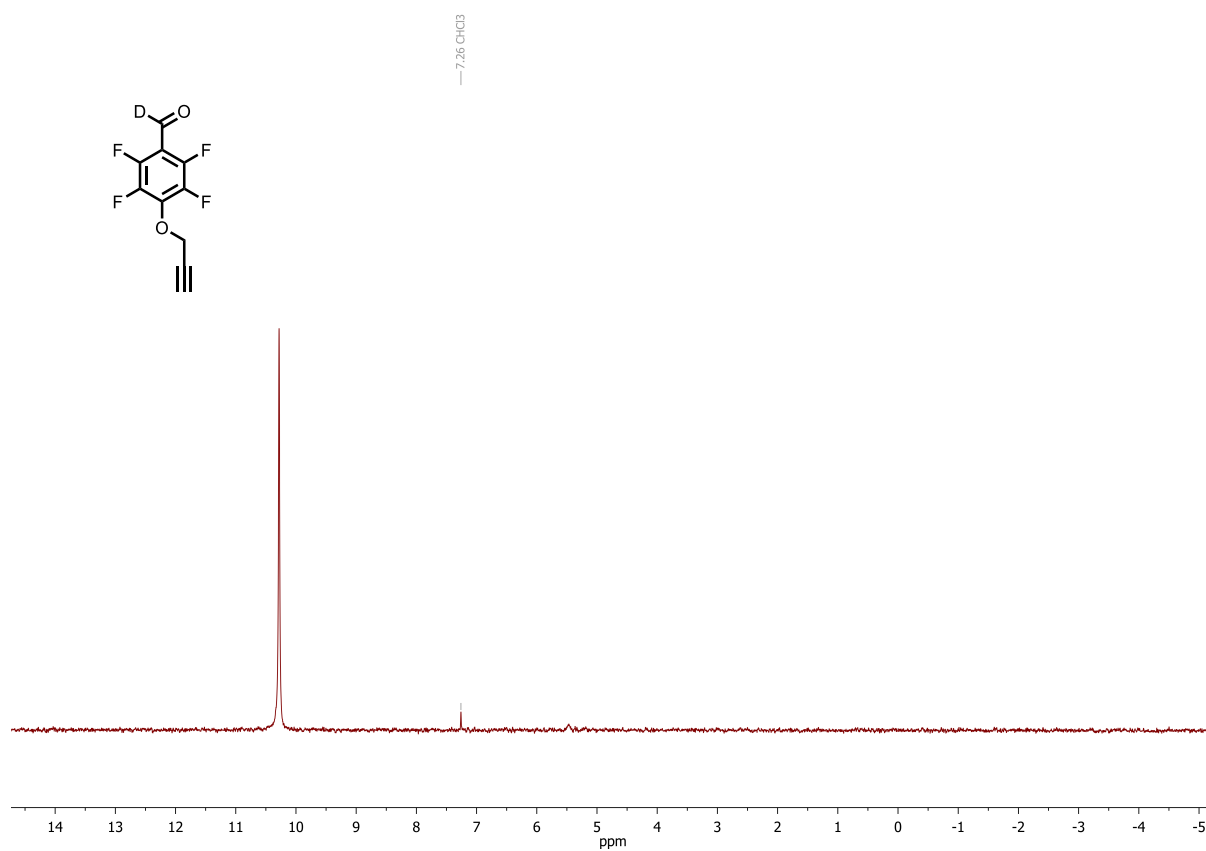
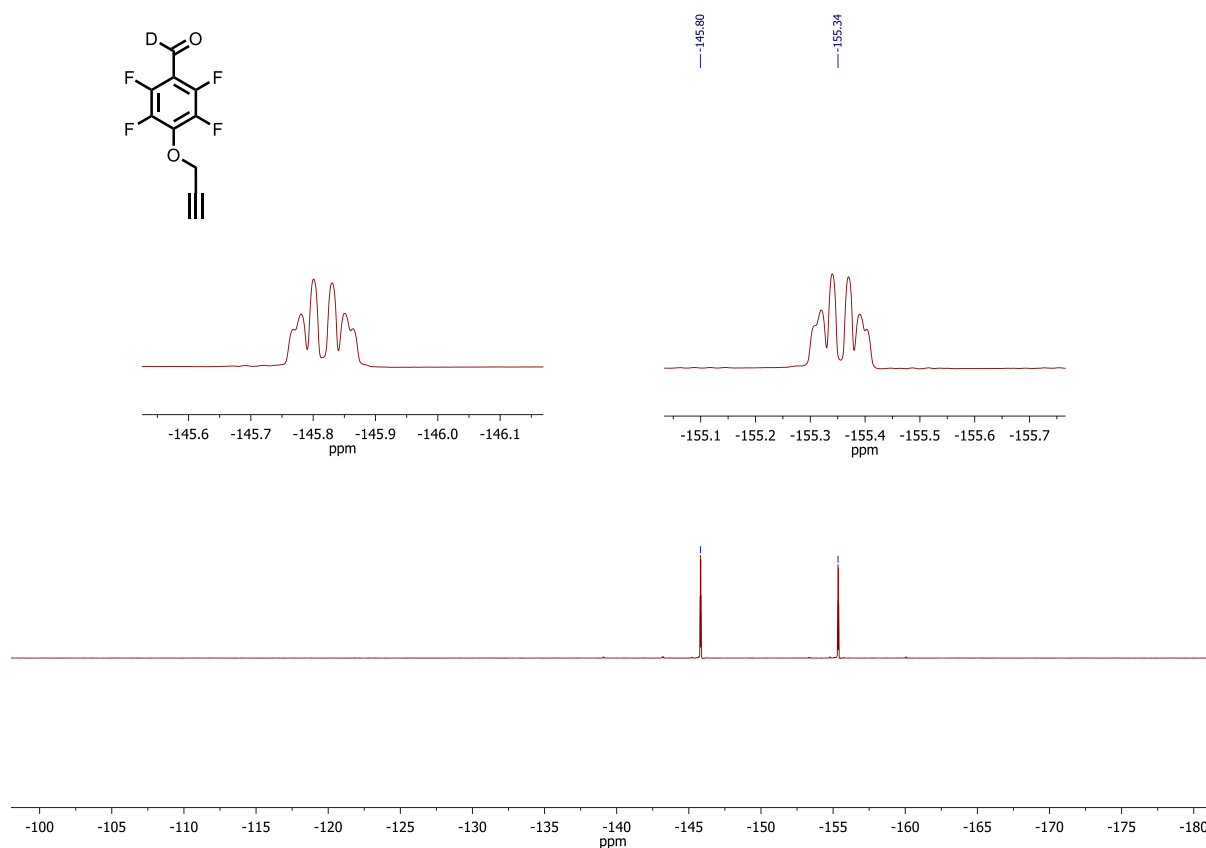
## 5.8 Spectra of S7



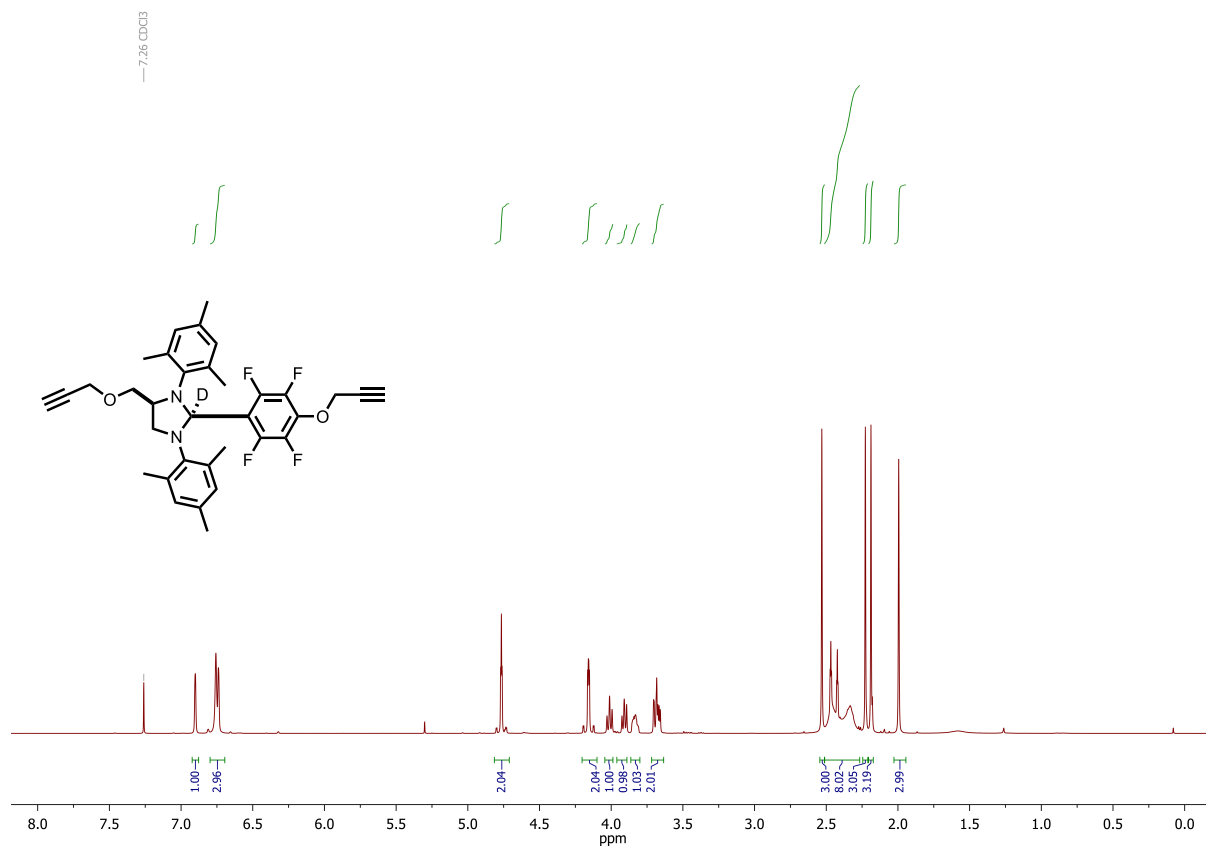
**Spectrum 21.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound **S7**.



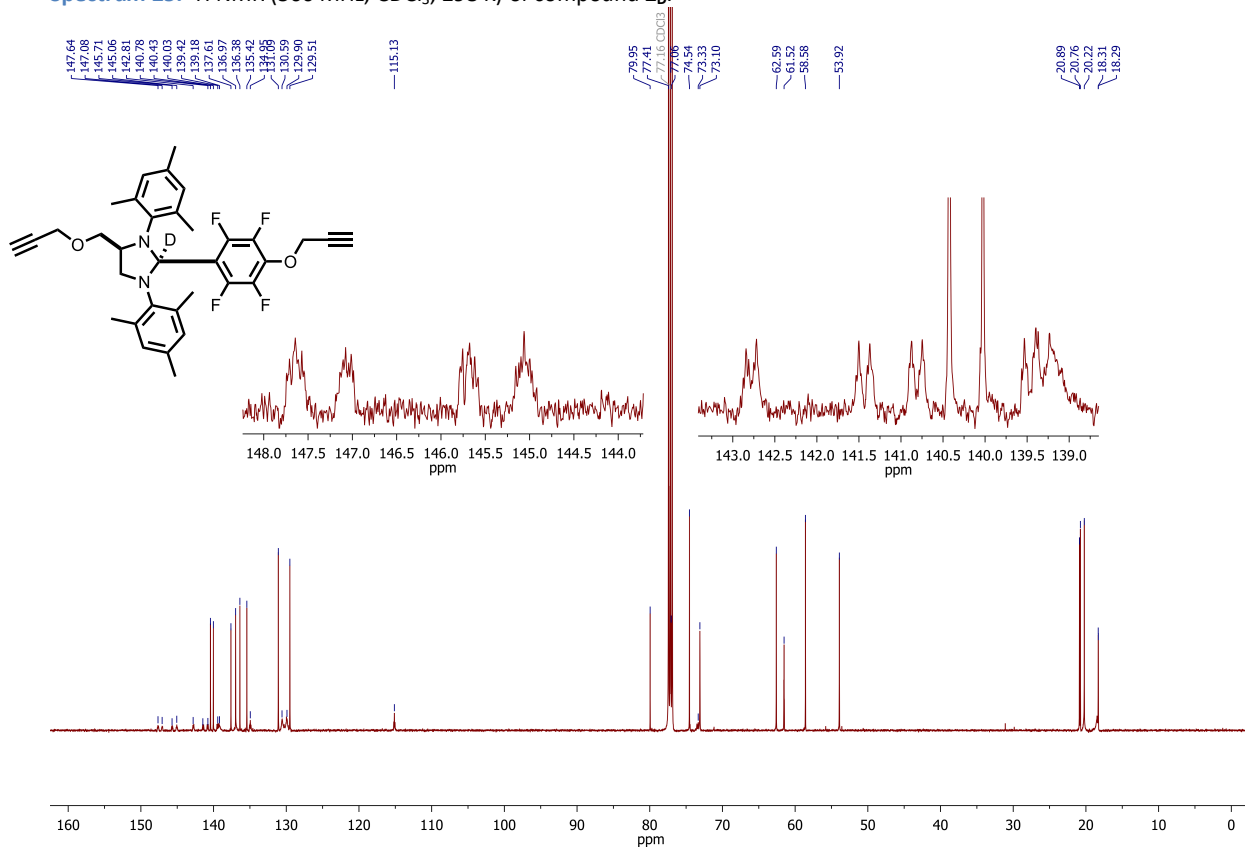
**Spectrum 22.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S7**.



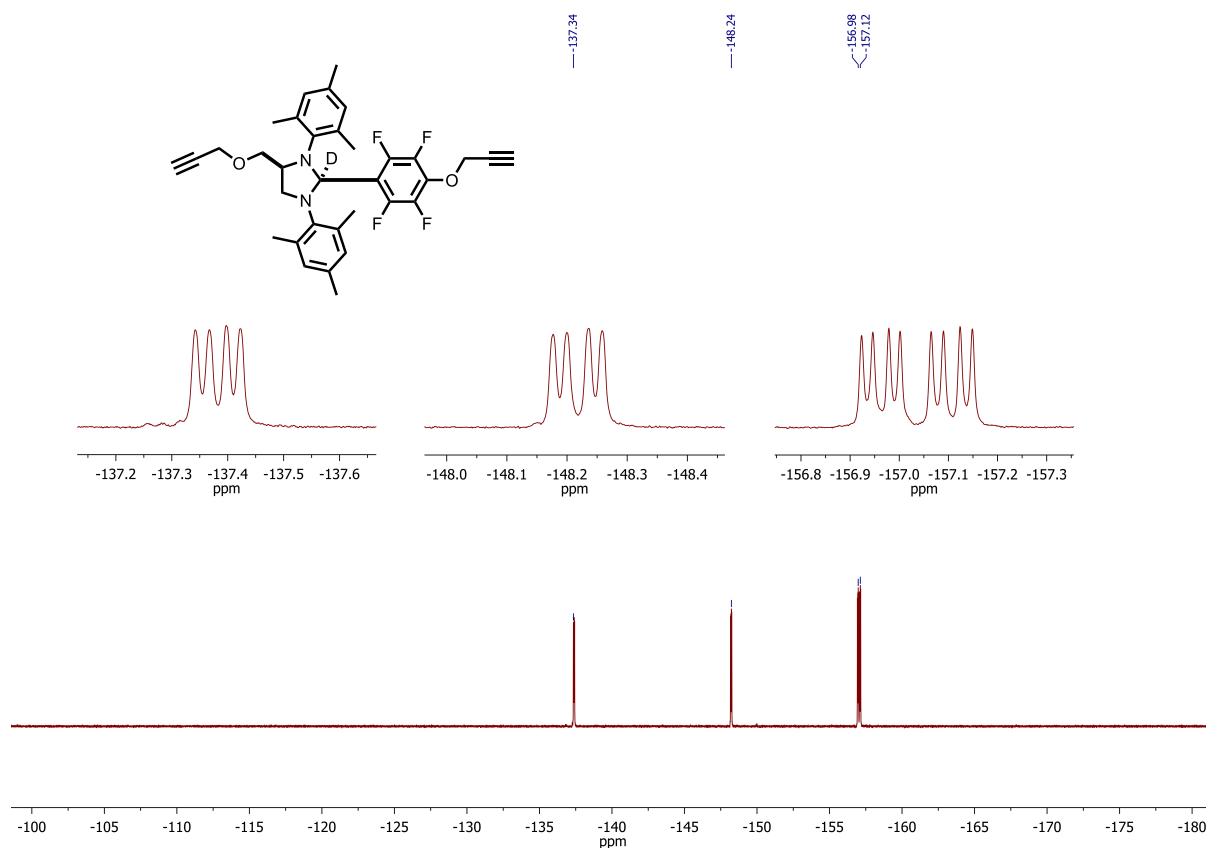
## 5.9 Spectra of 2<sub>D</sub>



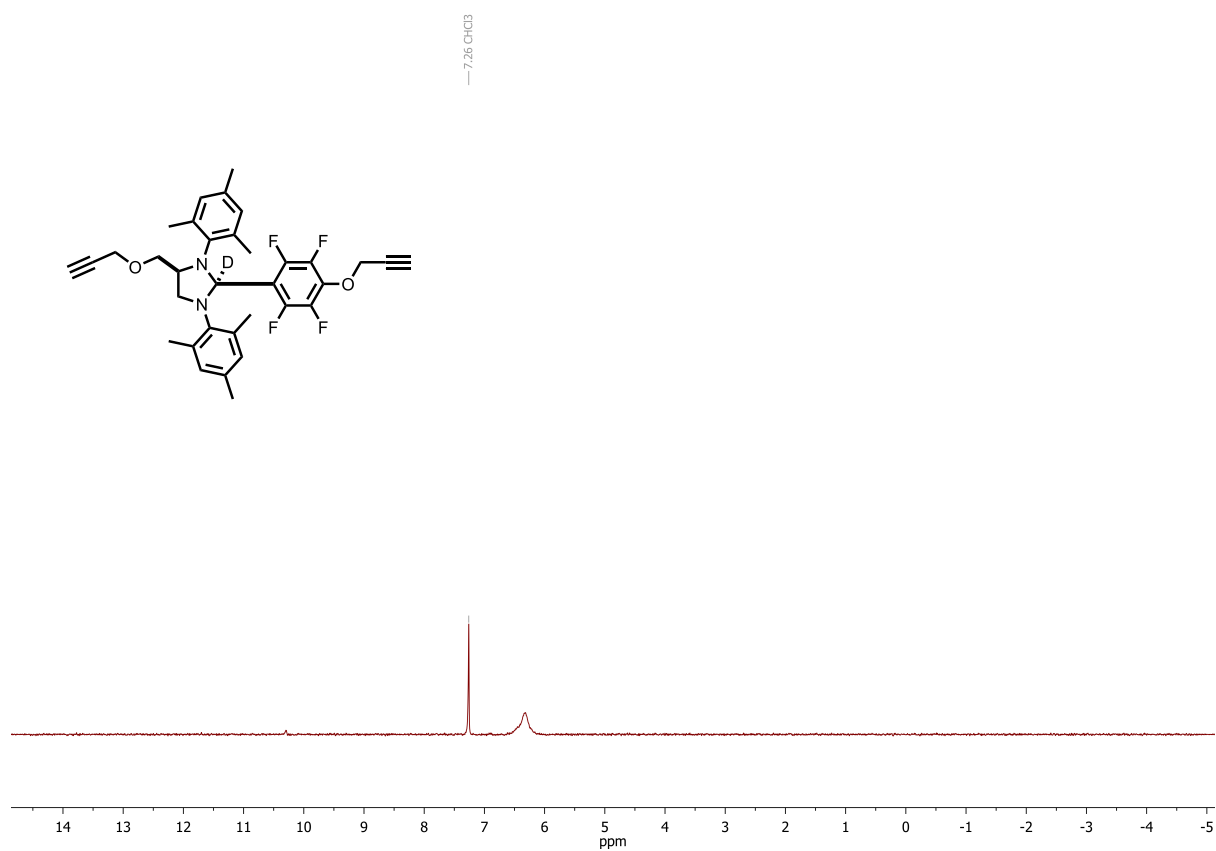
**Spectrum 25.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound 2<sub>D</sub>.



**Spectrum 26.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound 2<sub>D</sub>.

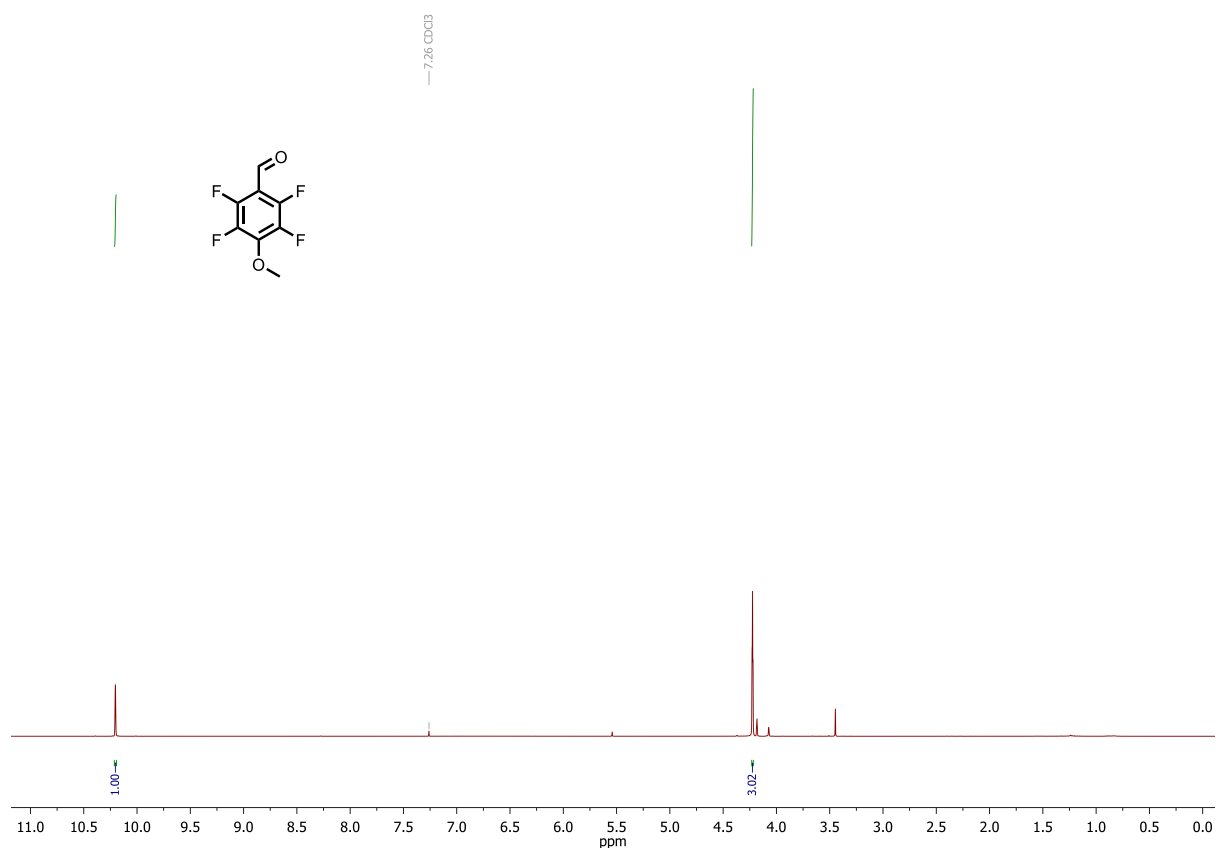


**Spectrum 27.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 298 K) of compound **2D**.

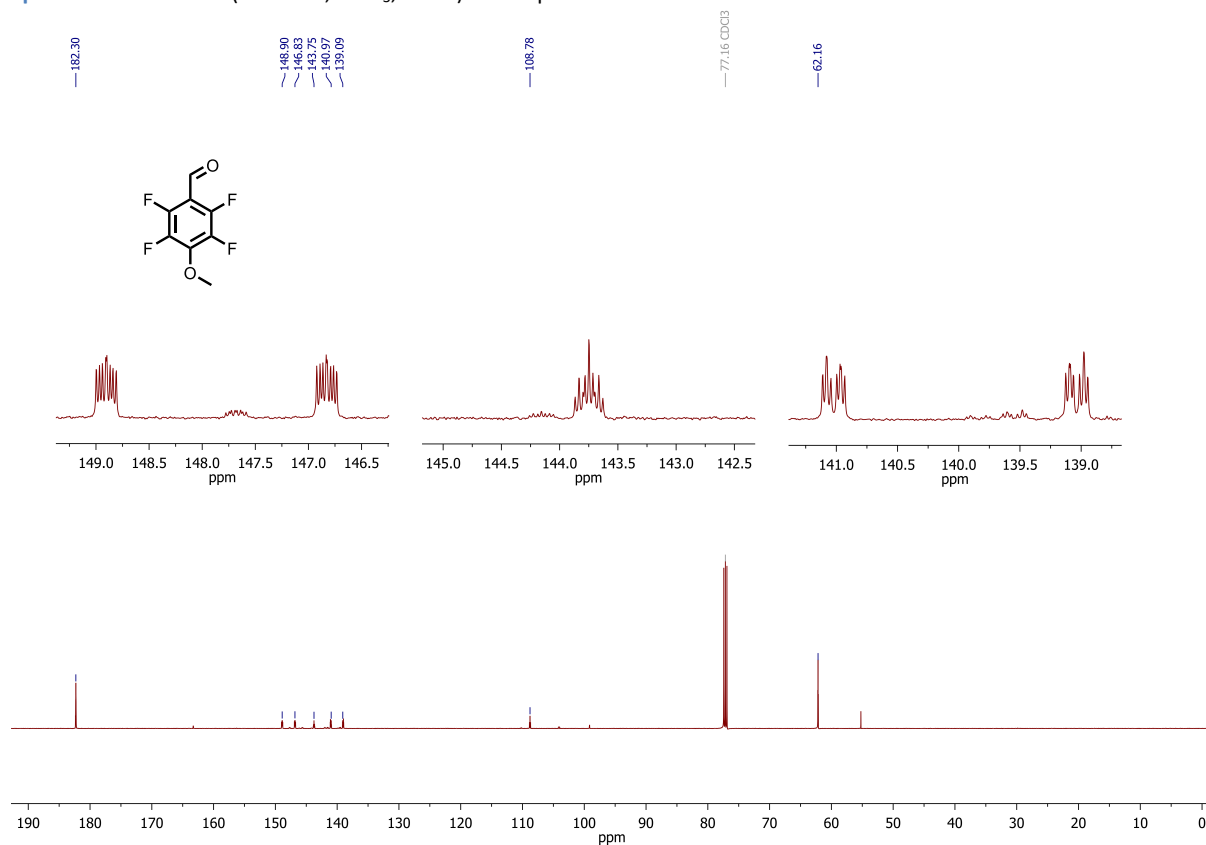


**Spectrum 28.**  $^1\text{H}$  NMR (77 MHz,  $\text{CHCl}_3$ , 298 K) of compound **2D**.

## 5.10 Spectra of S8

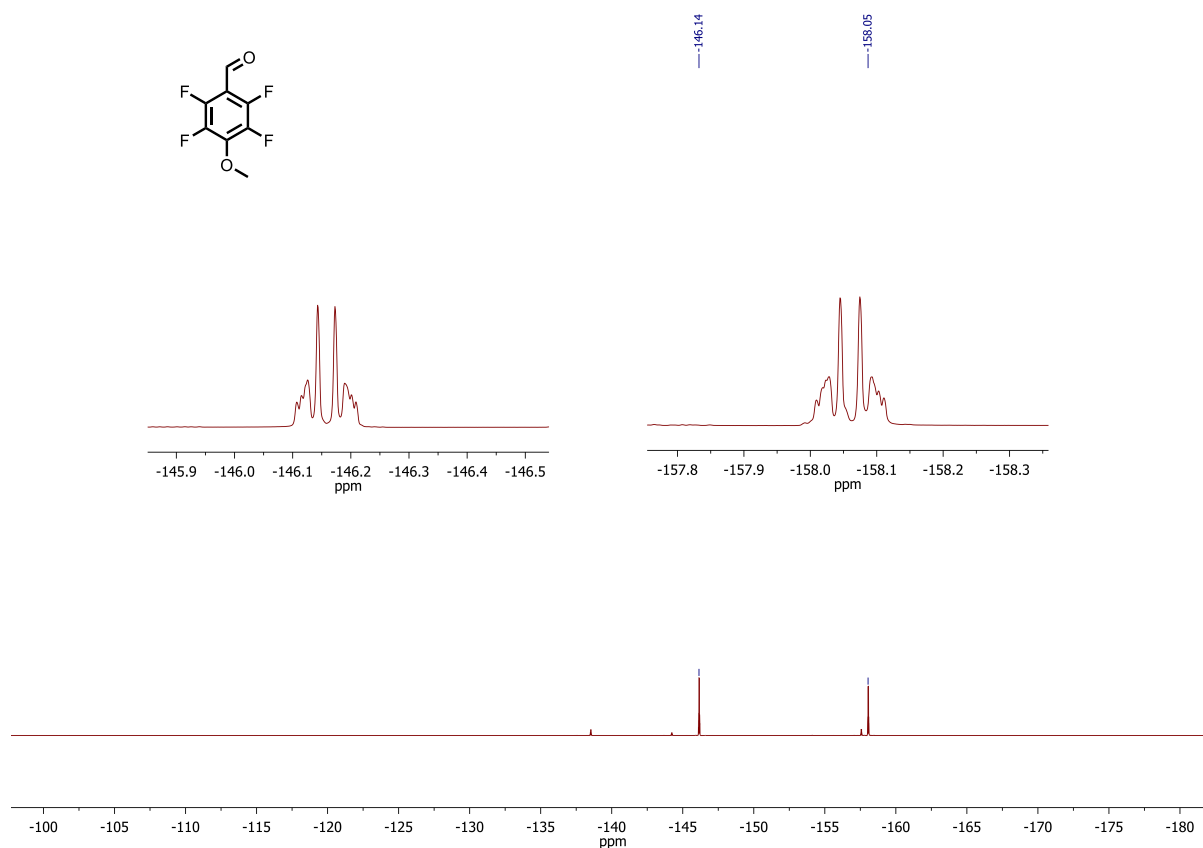


**Spectrum 29.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S8**.

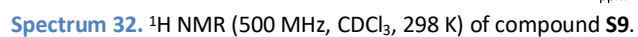


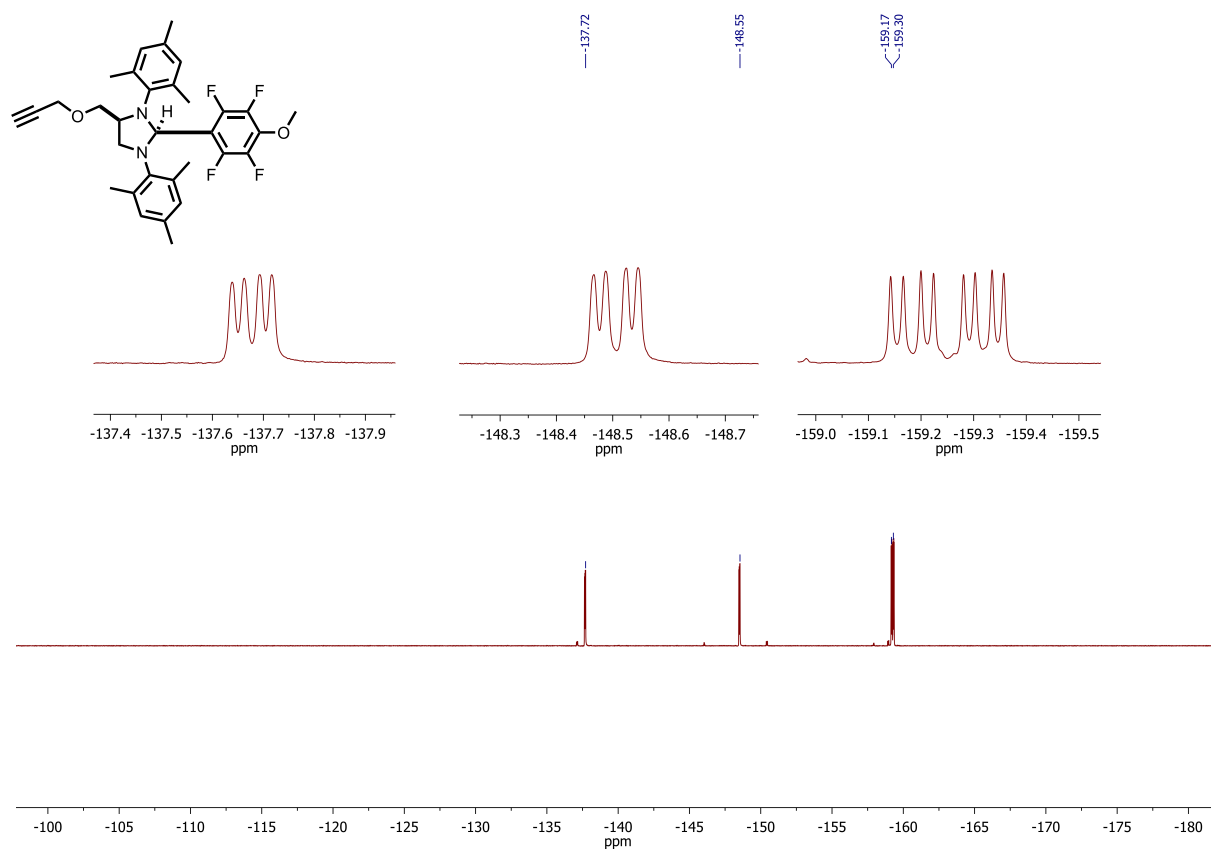
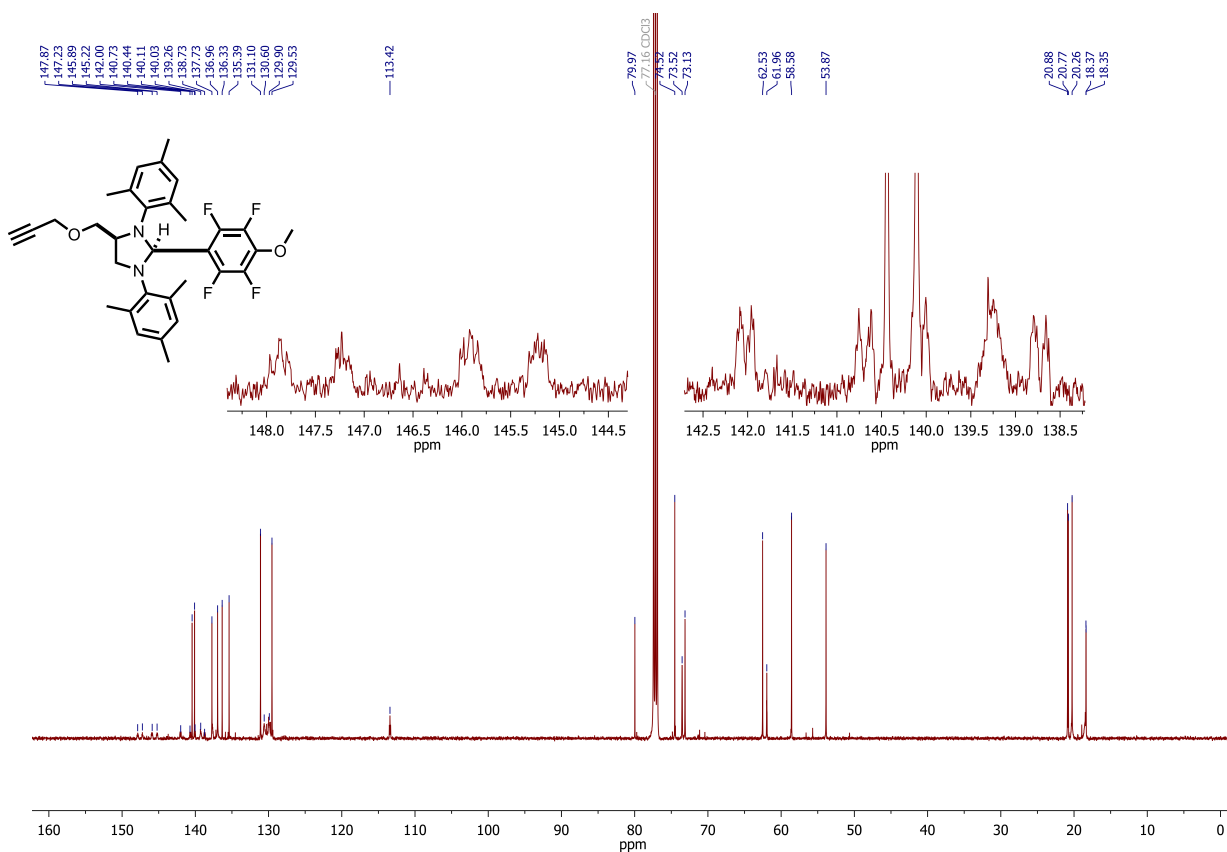
**Spectrum 30.**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S8**.



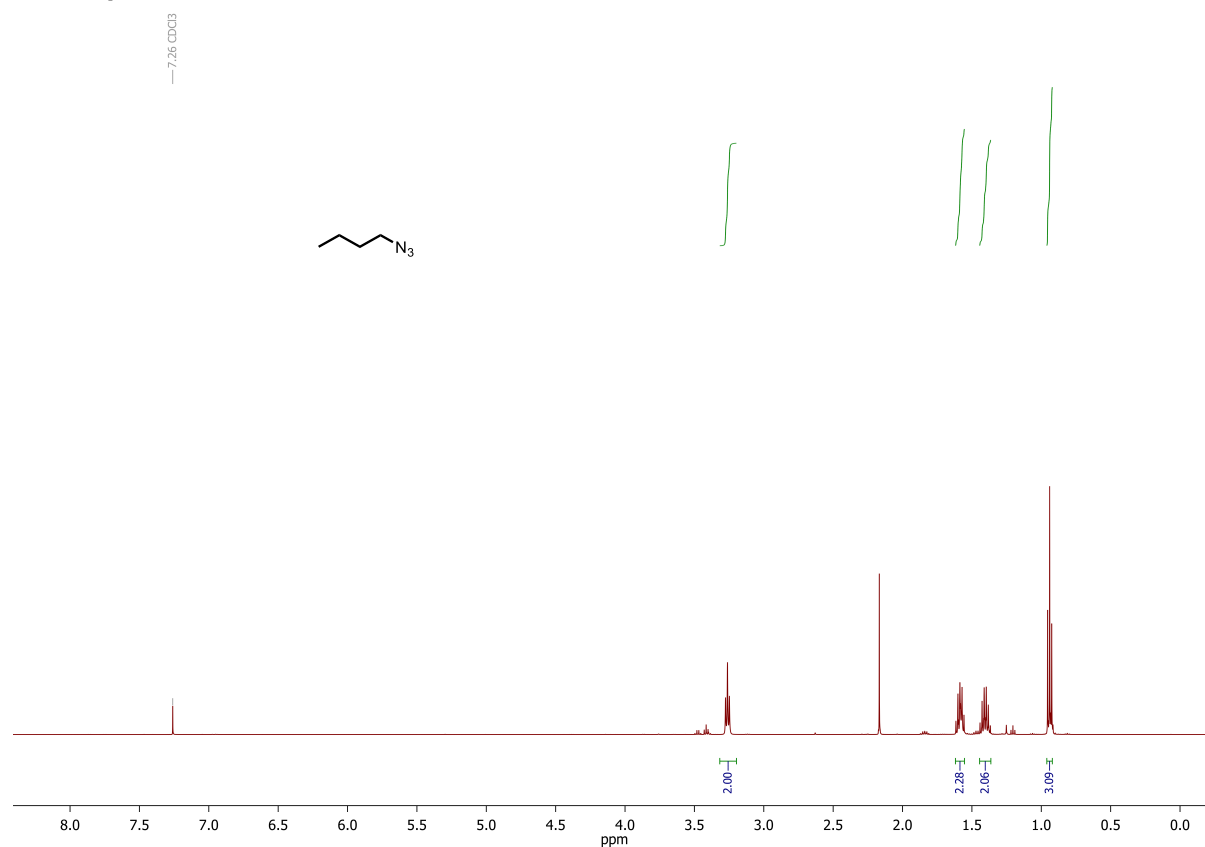


### 5.11 Spectra of S9

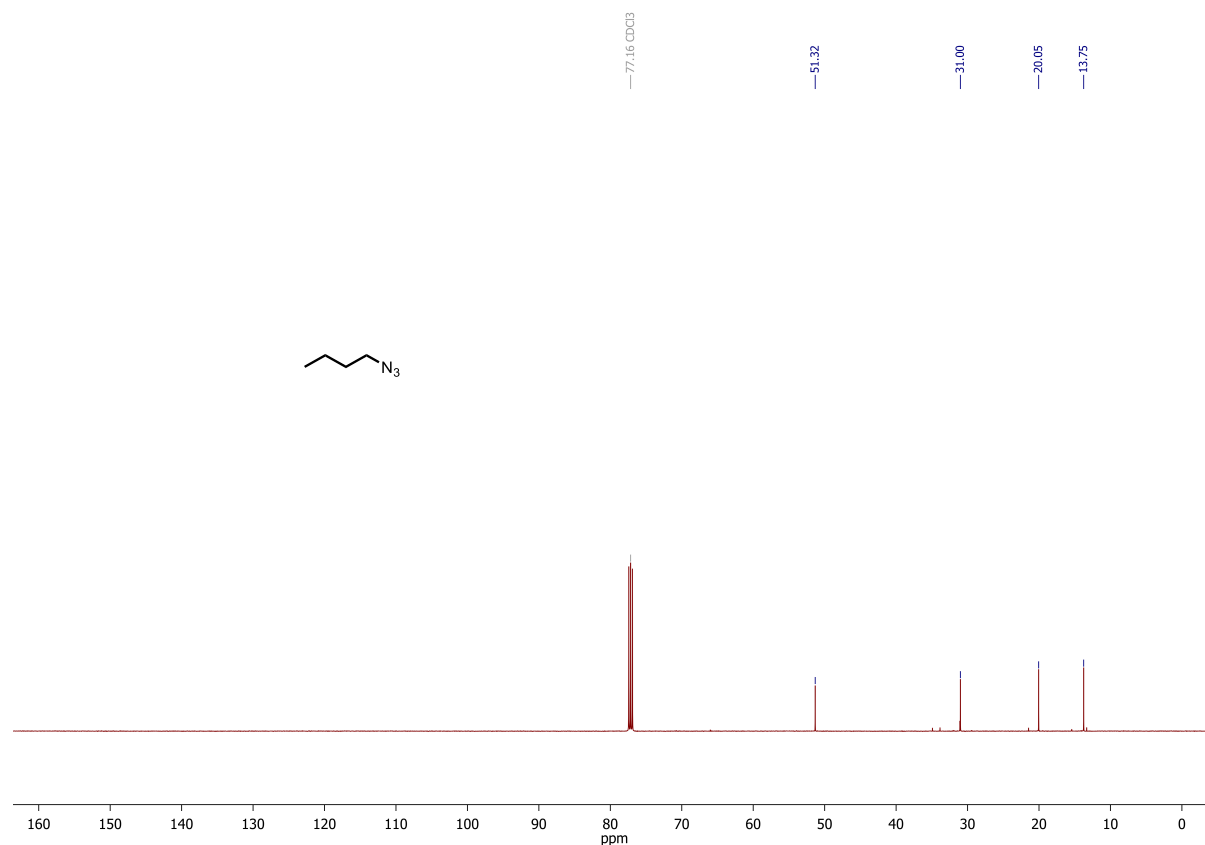




## 5.12 Spectra of S10

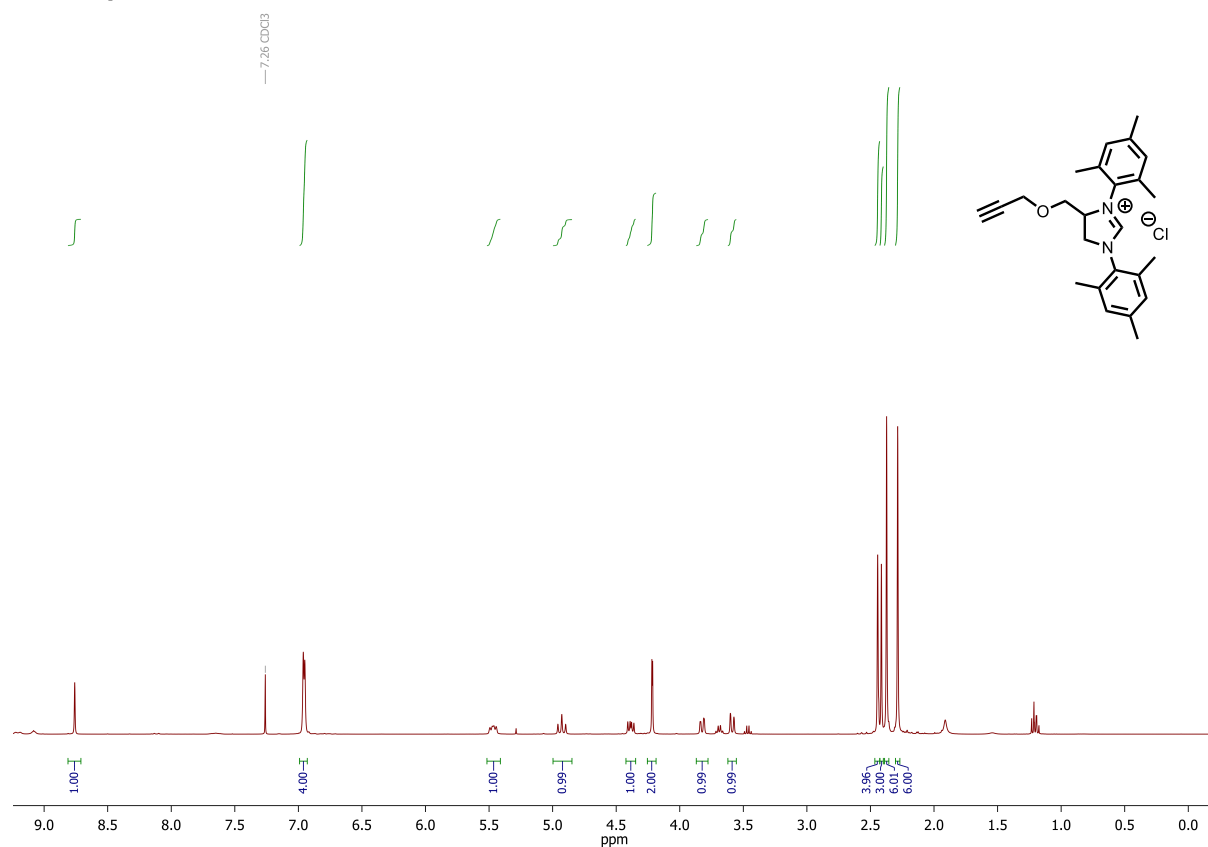


**Spectrum 35.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of compound S10.

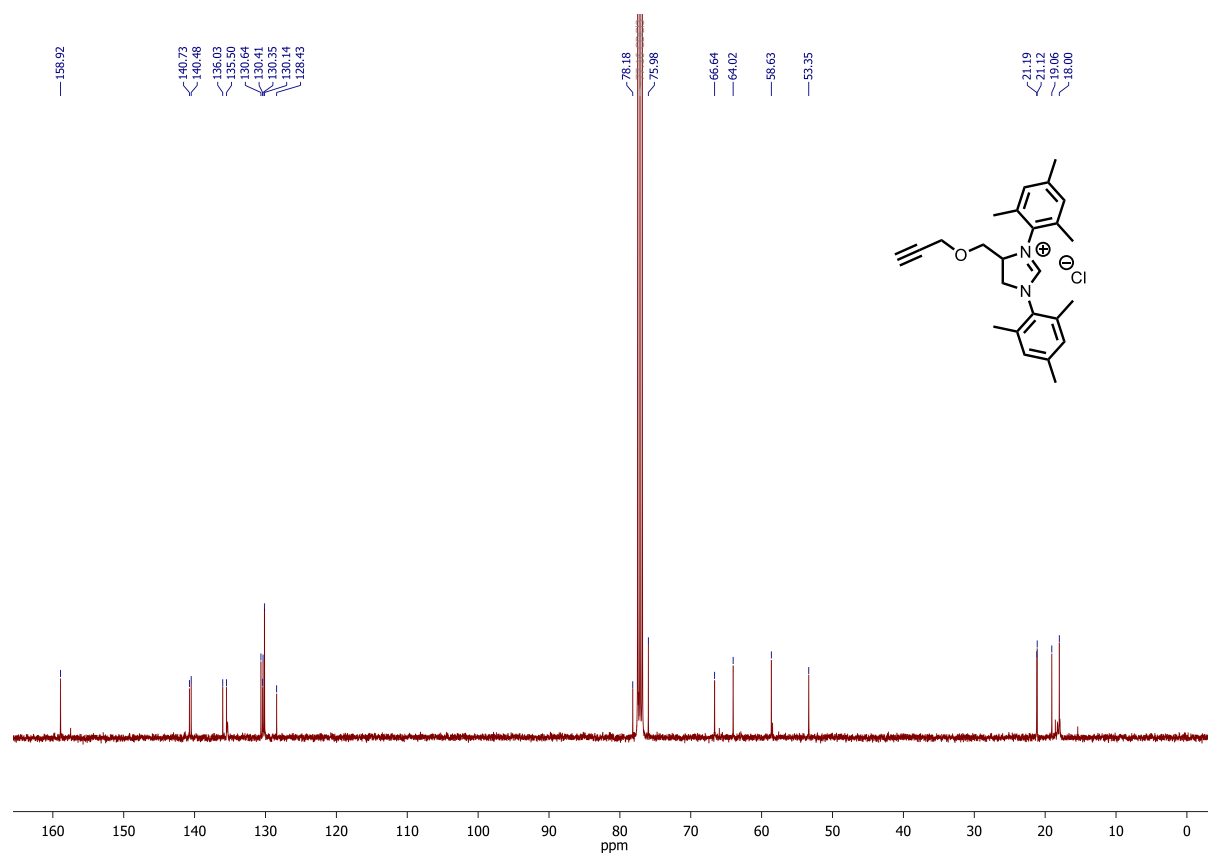


**Spectrum 36.**  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K) of compound S10.

## 5.13 Spectra of S11

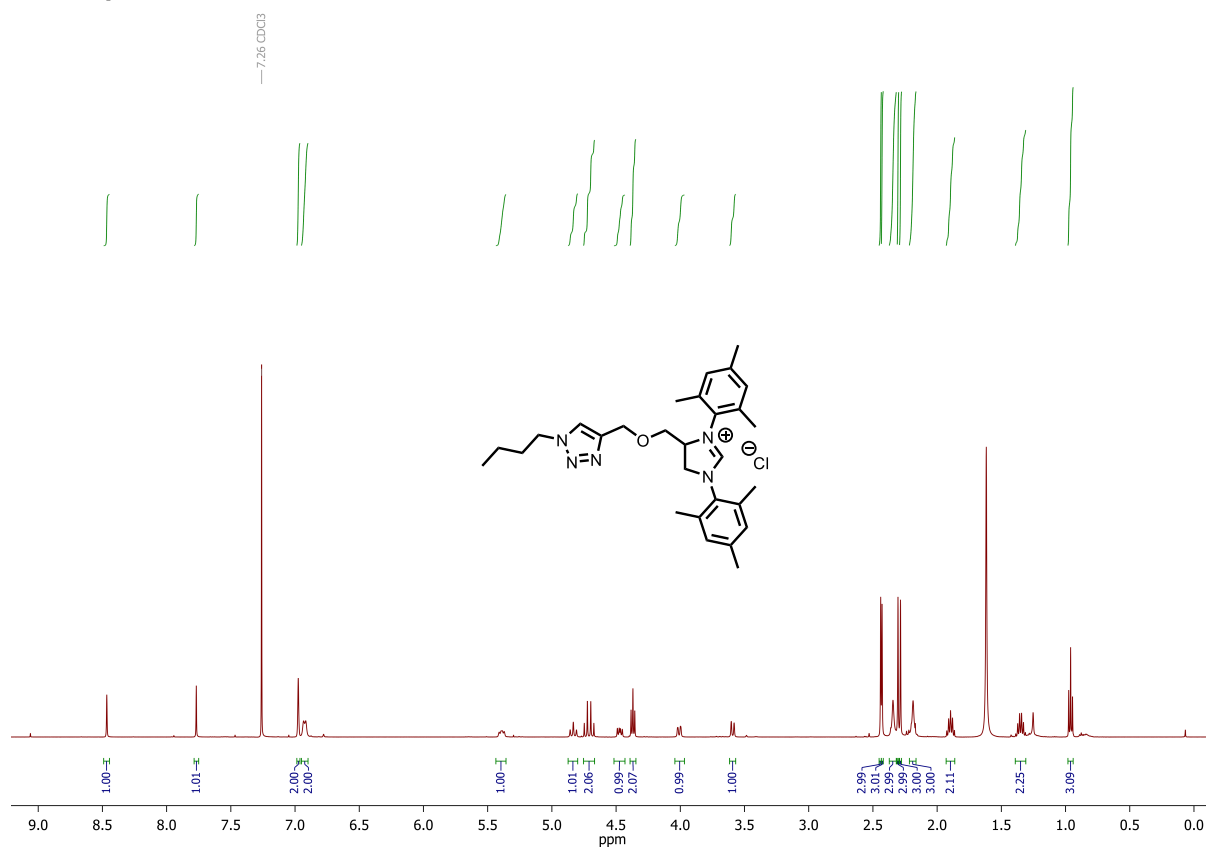


**Spectrum 37.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) of compound **S11**.

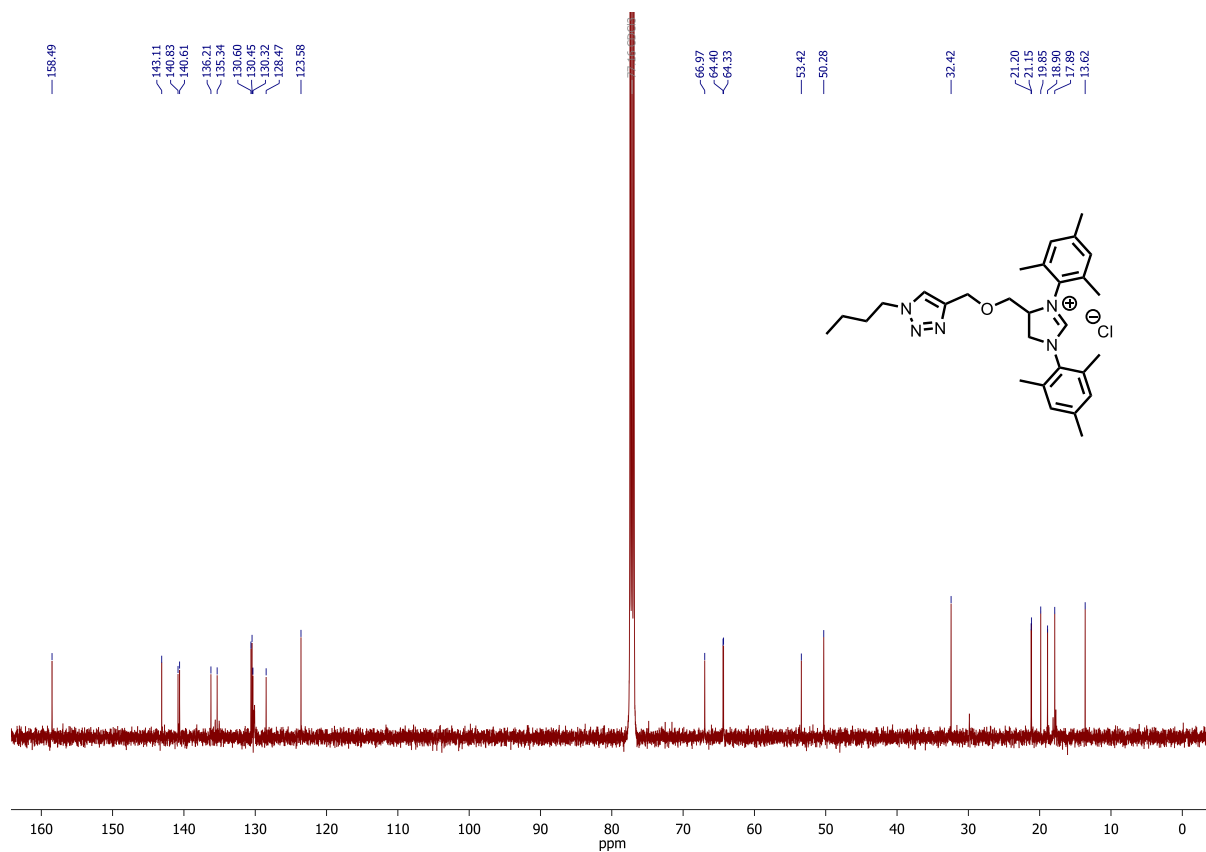


**Spectrum 38.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 298 K) of compound **S11**.

## 5.14 Spectra of **6<sub>ref</sub>**

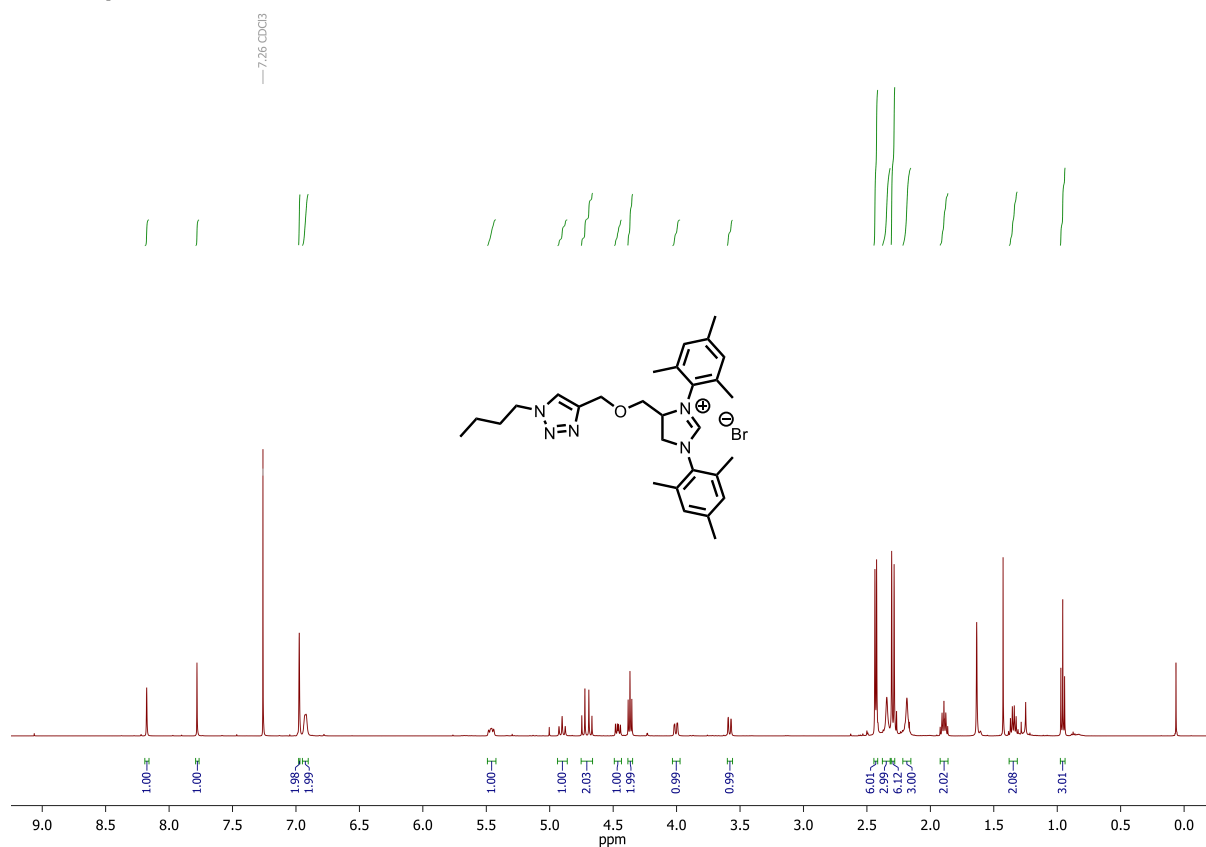


**Spectrum 39.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **6<sub>ref</sub>**.

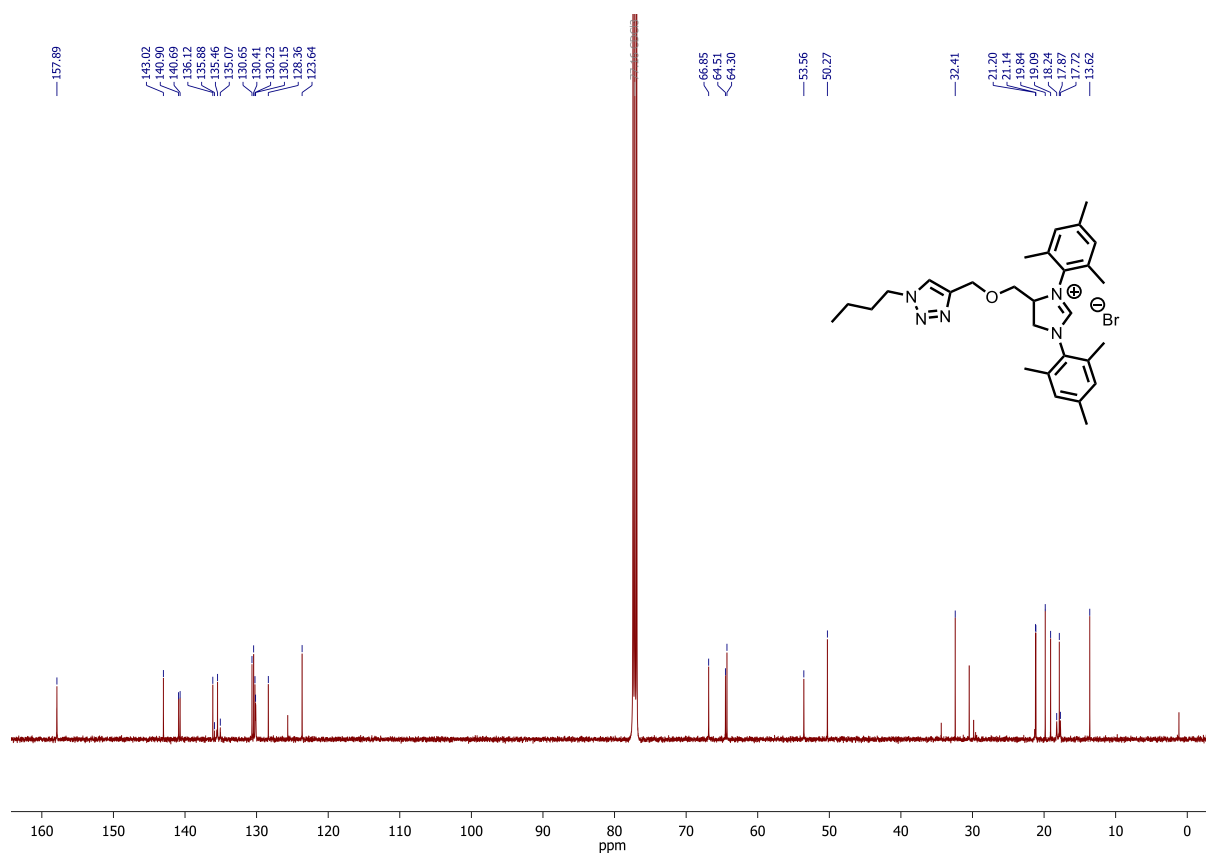


**Spectrum 40.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **6<sub>ref</sub>**.

## 5.15 Spectra of S12

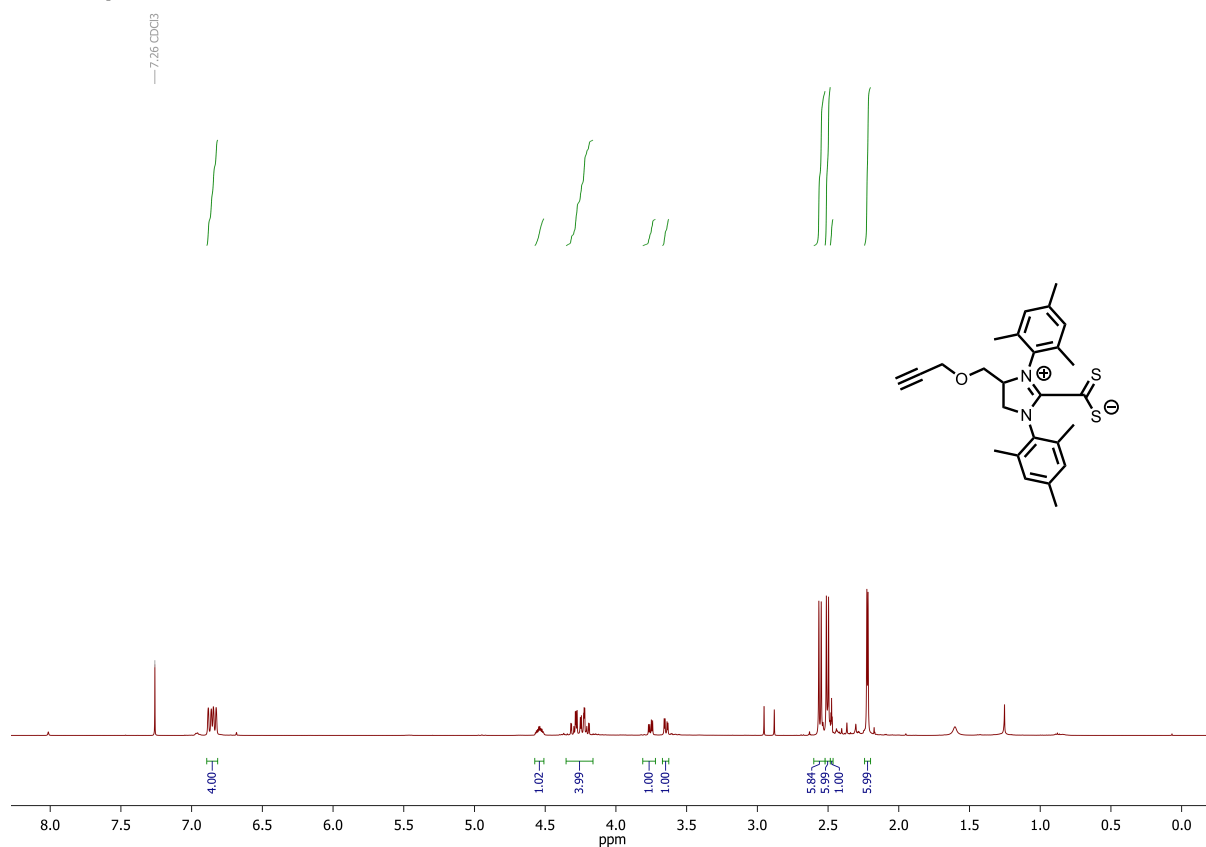


**Spectrum 41.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **S12**.

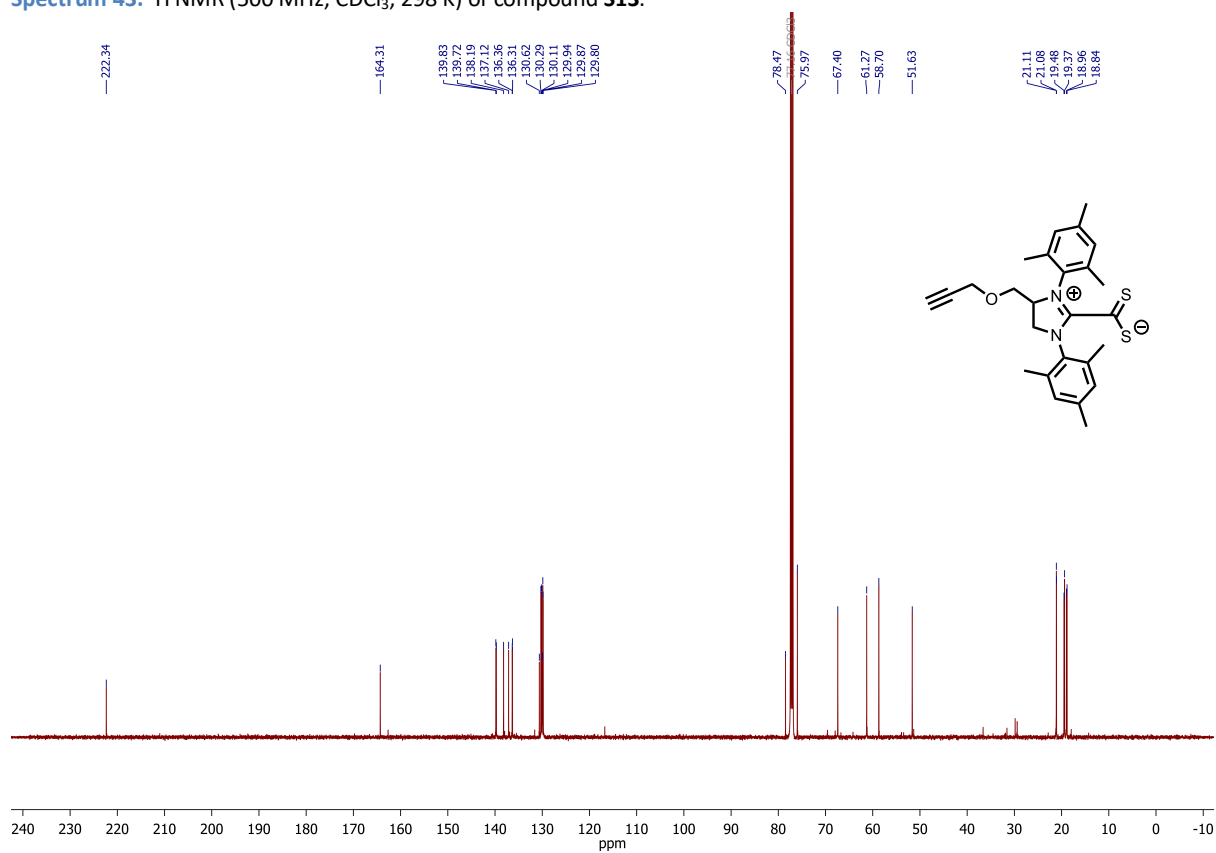


**Spectrum 42.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S12**.

## 5.16 Spectra of S13

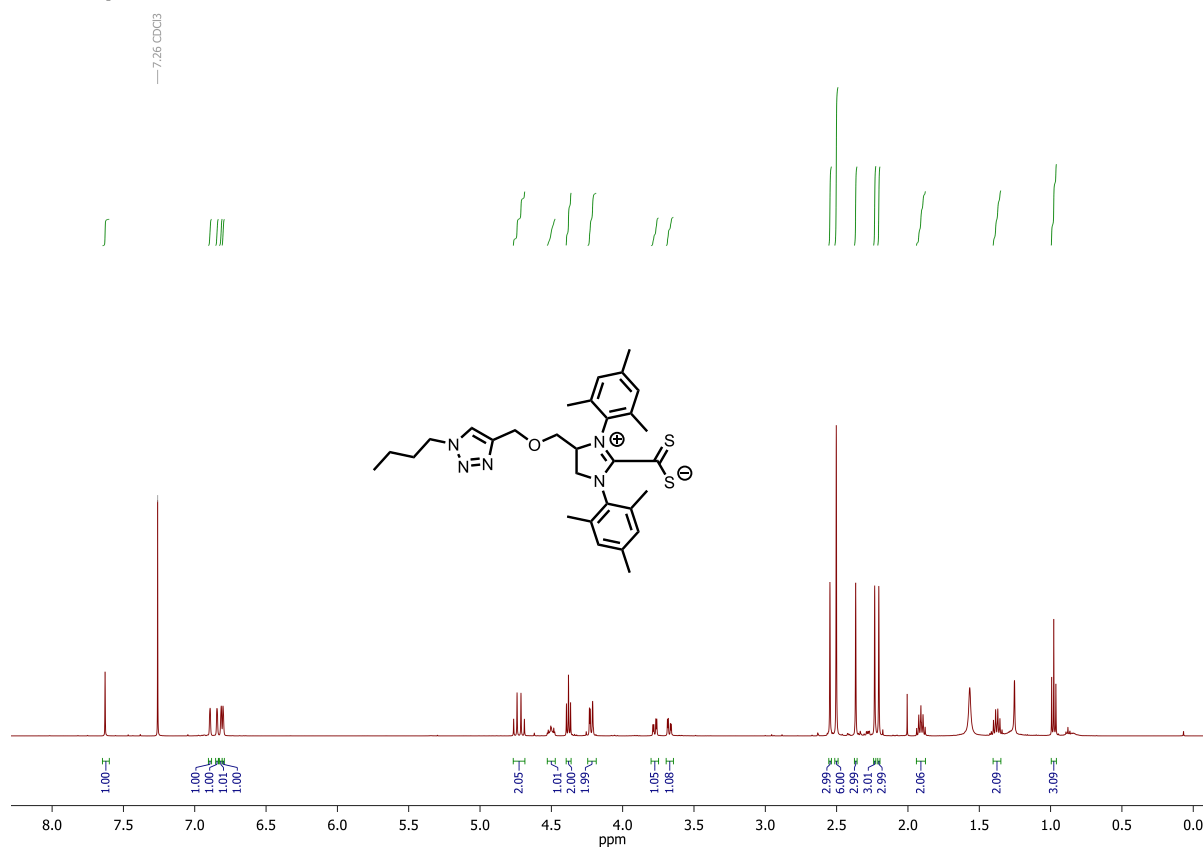


**Spectrum 43.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **S13**.

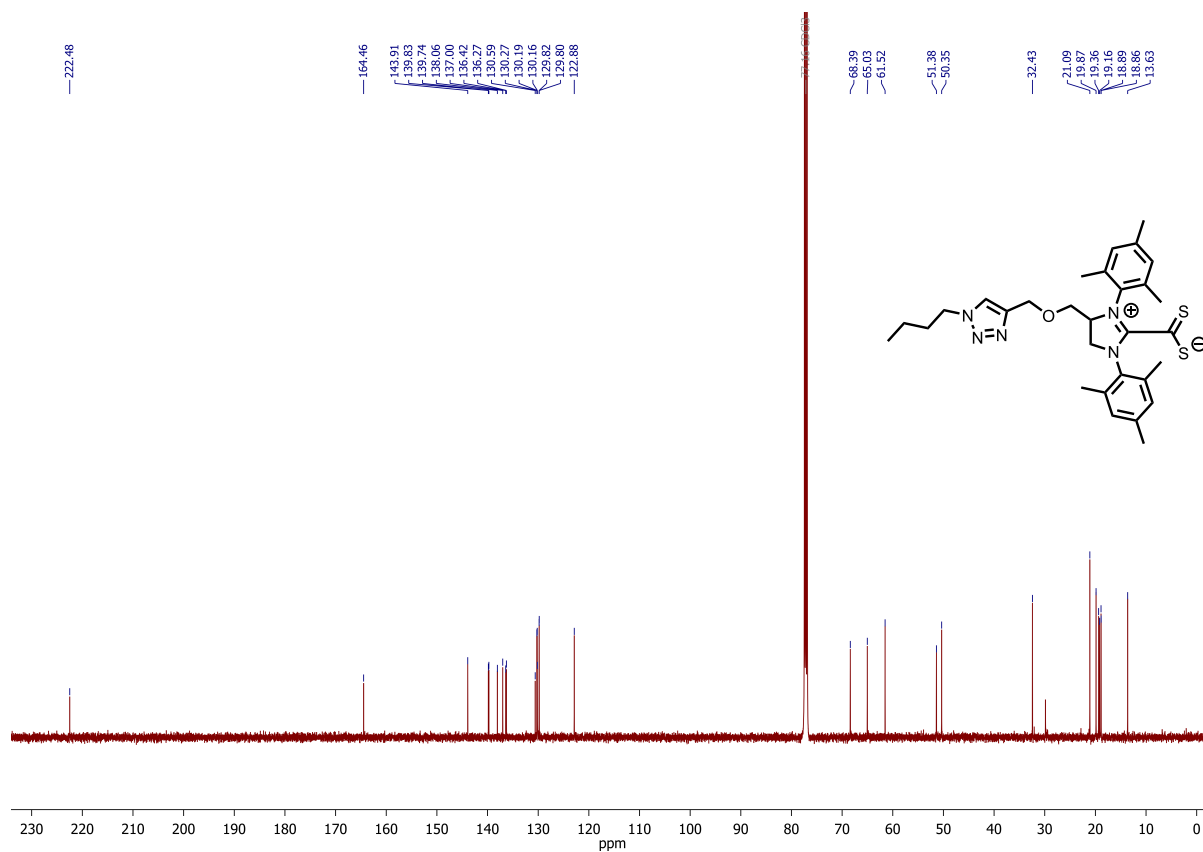


**Spectrum 44.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S13**.

## 5.17 Spectra of **7<sub>ref</sub>**



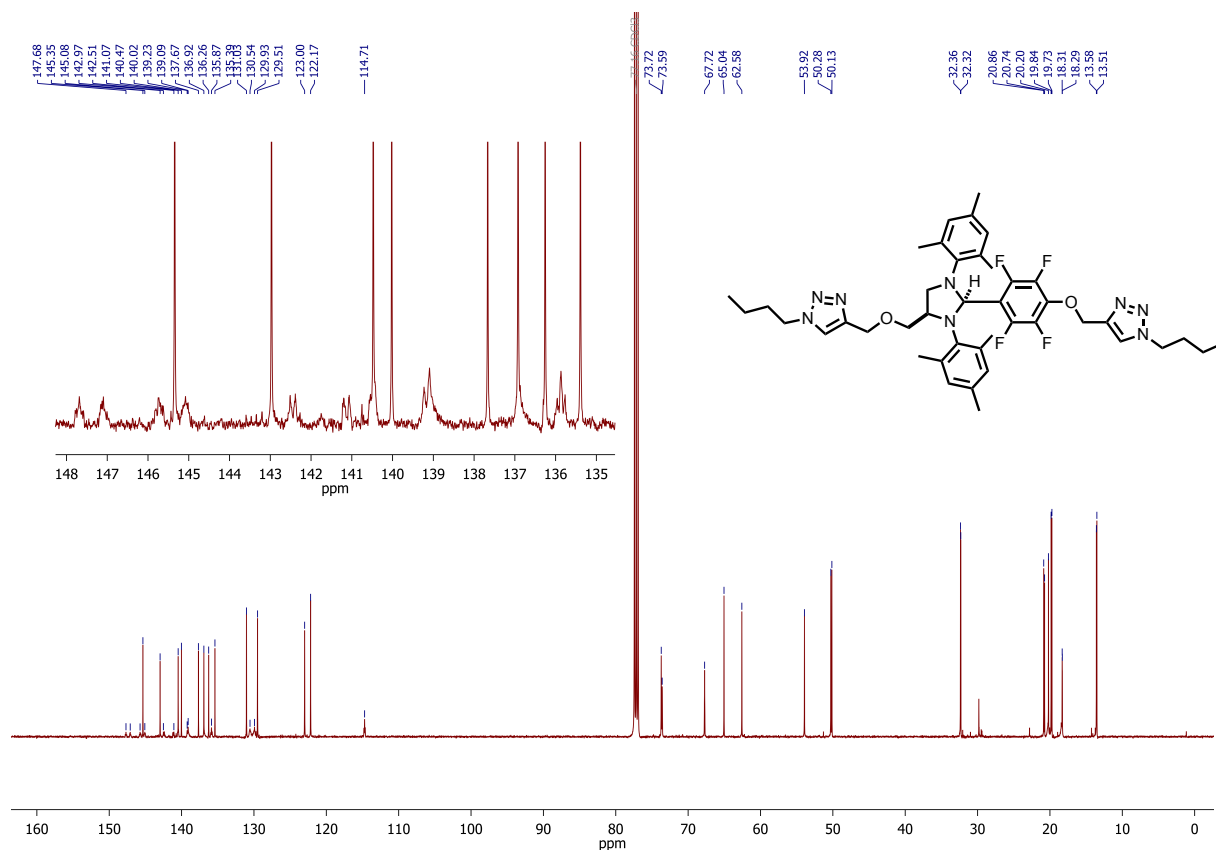
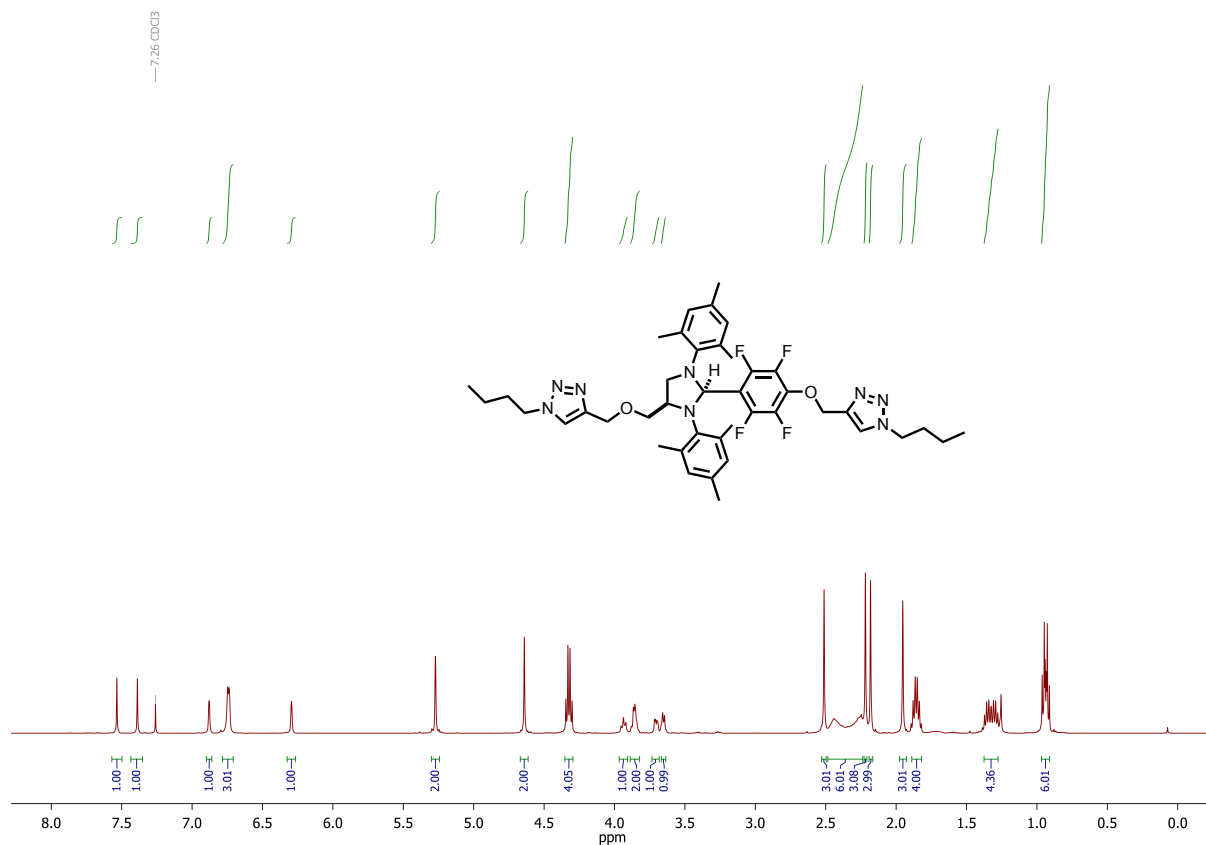
**Spectrum 45.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **7<sub>ref</sub>**.

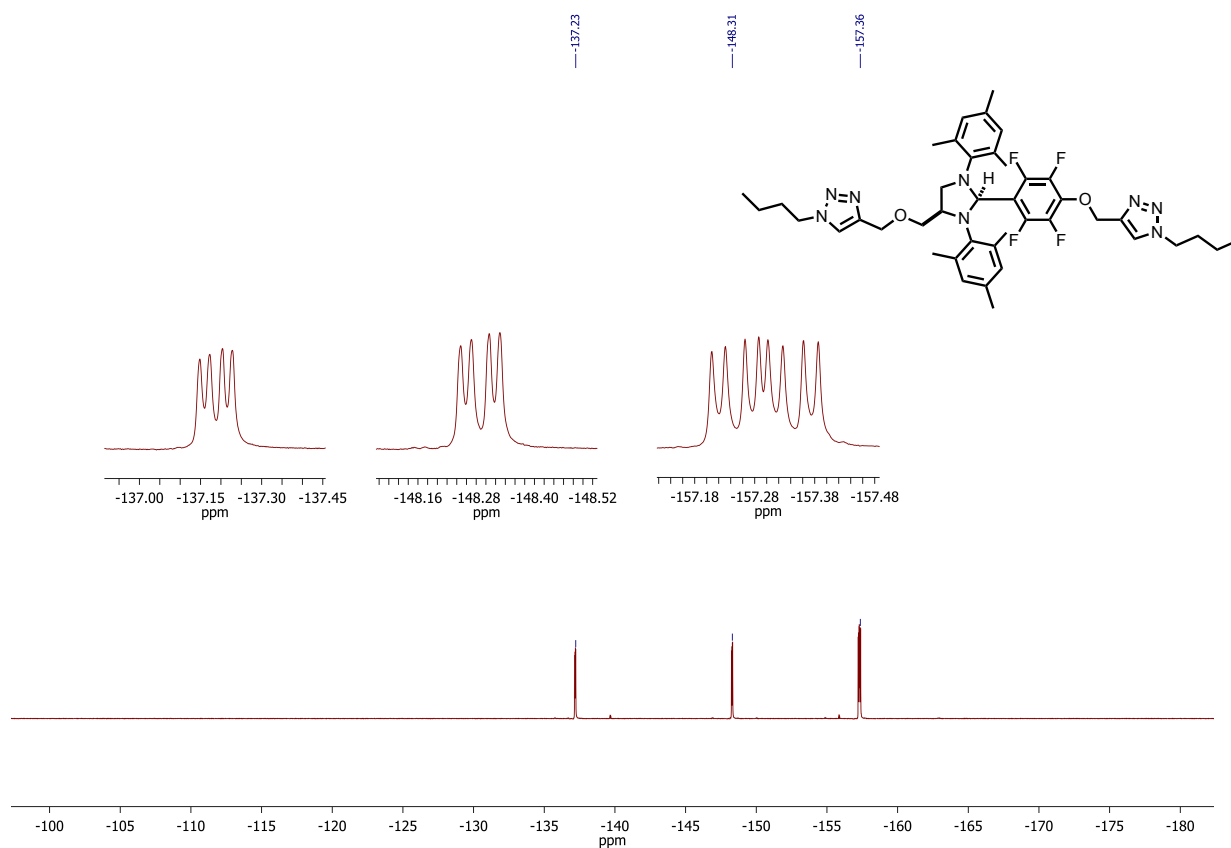


**Spectrum 46.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **7<sub>ref</sub>**.



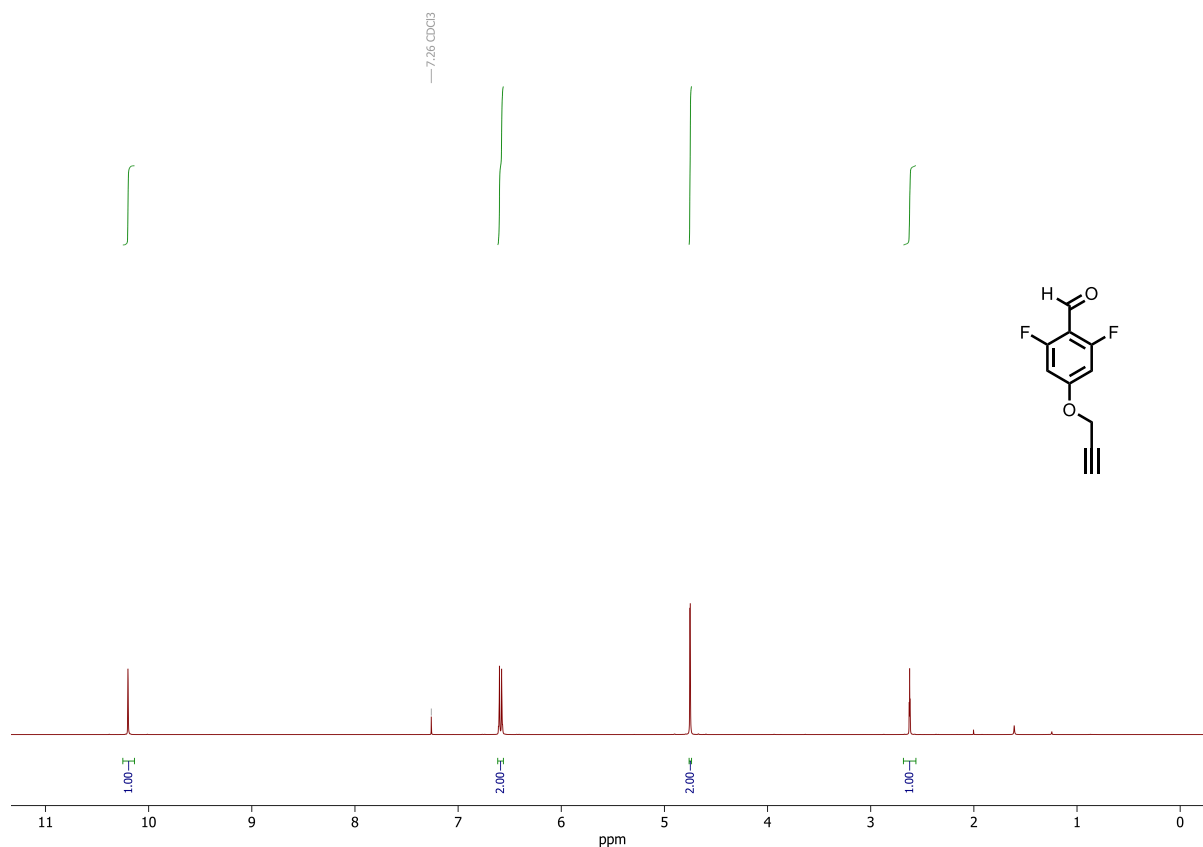
## 5.18 Spectra of S14



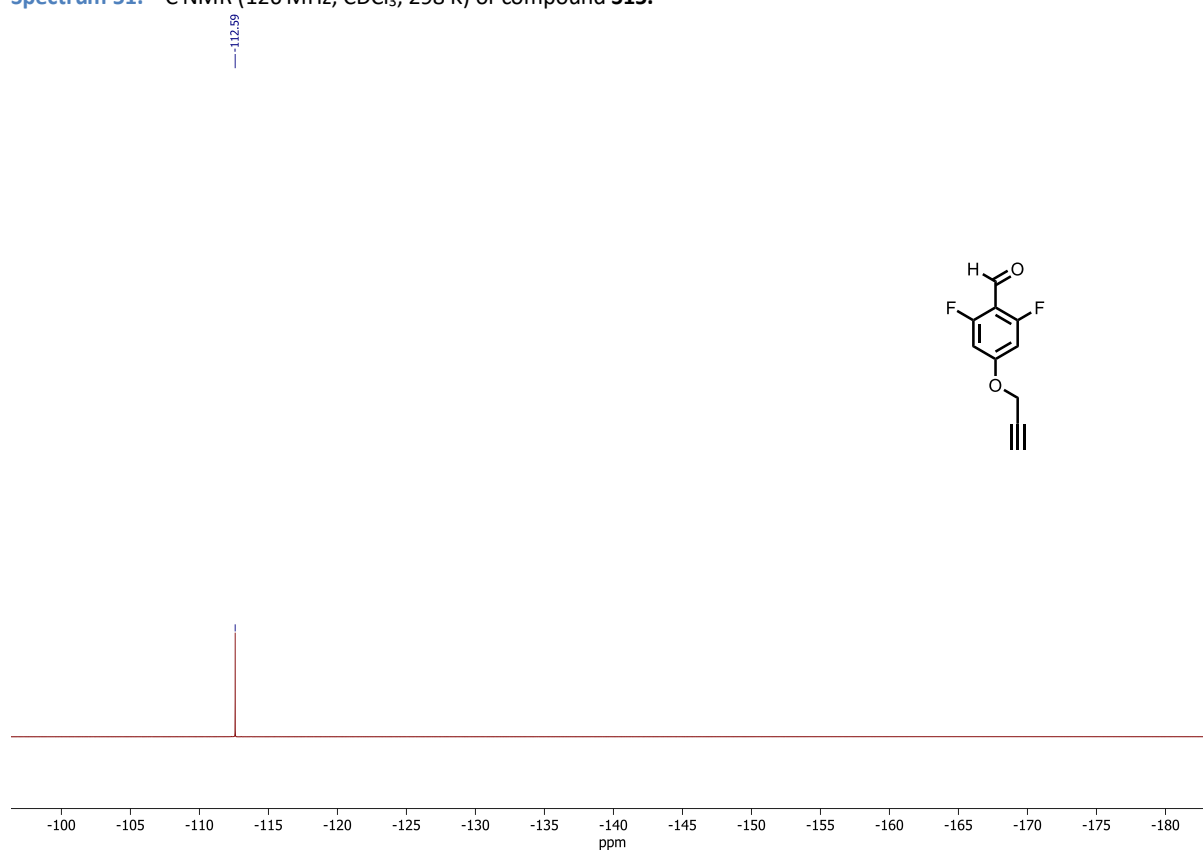
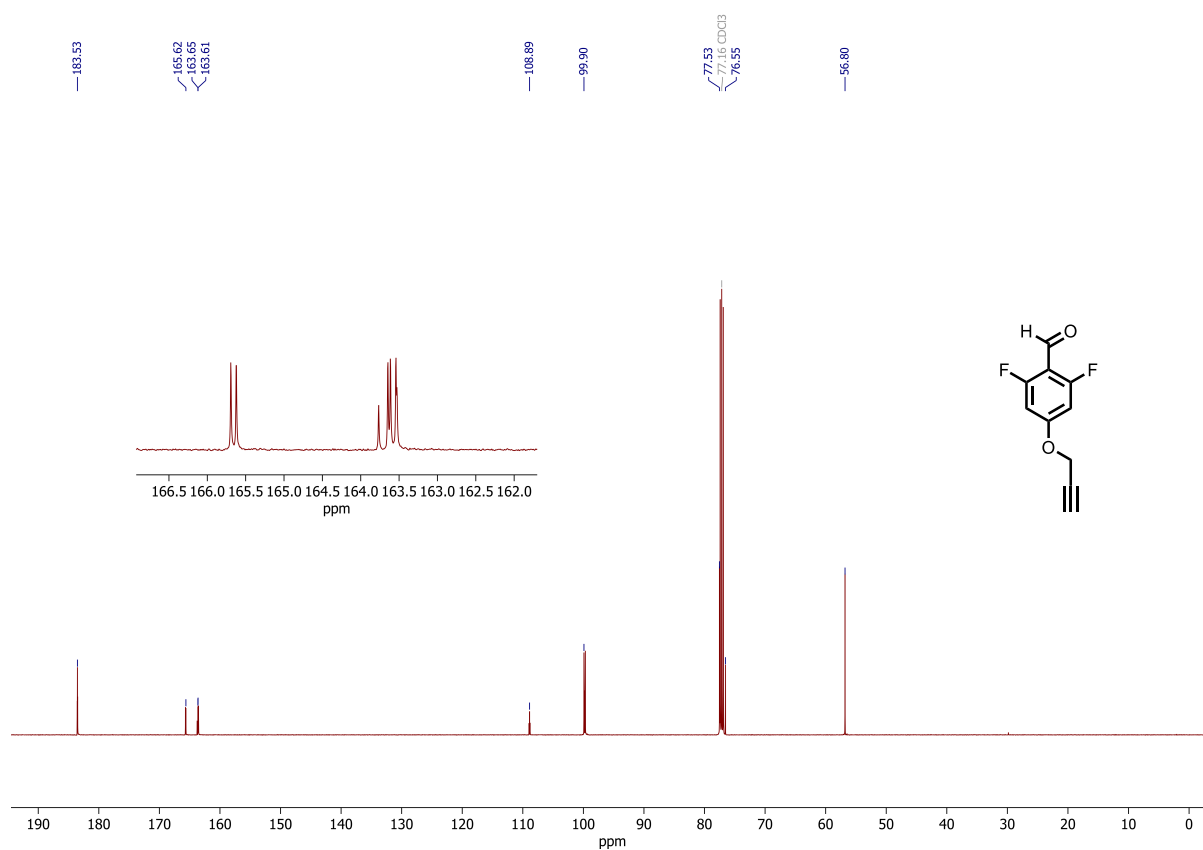


**Spectrum 49.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S14**.

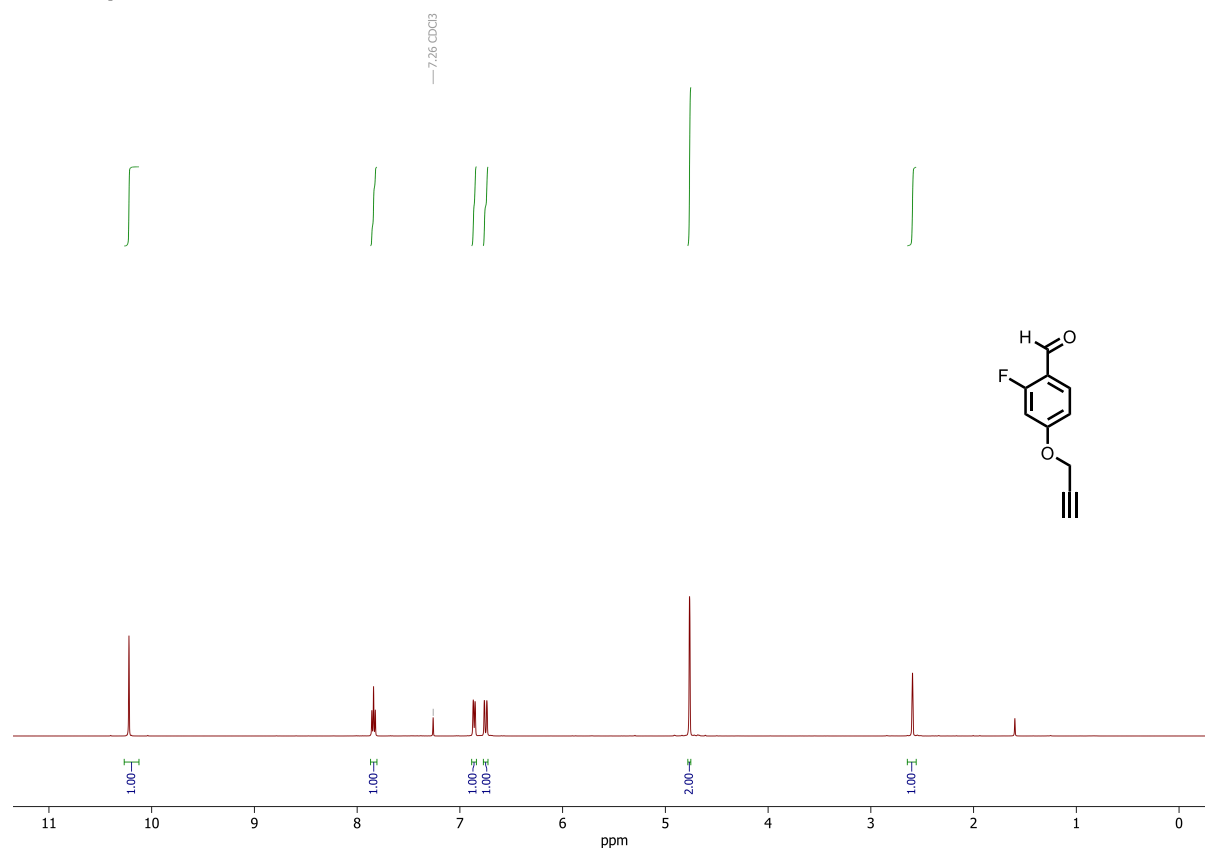
## 5.19 Spectra of S15



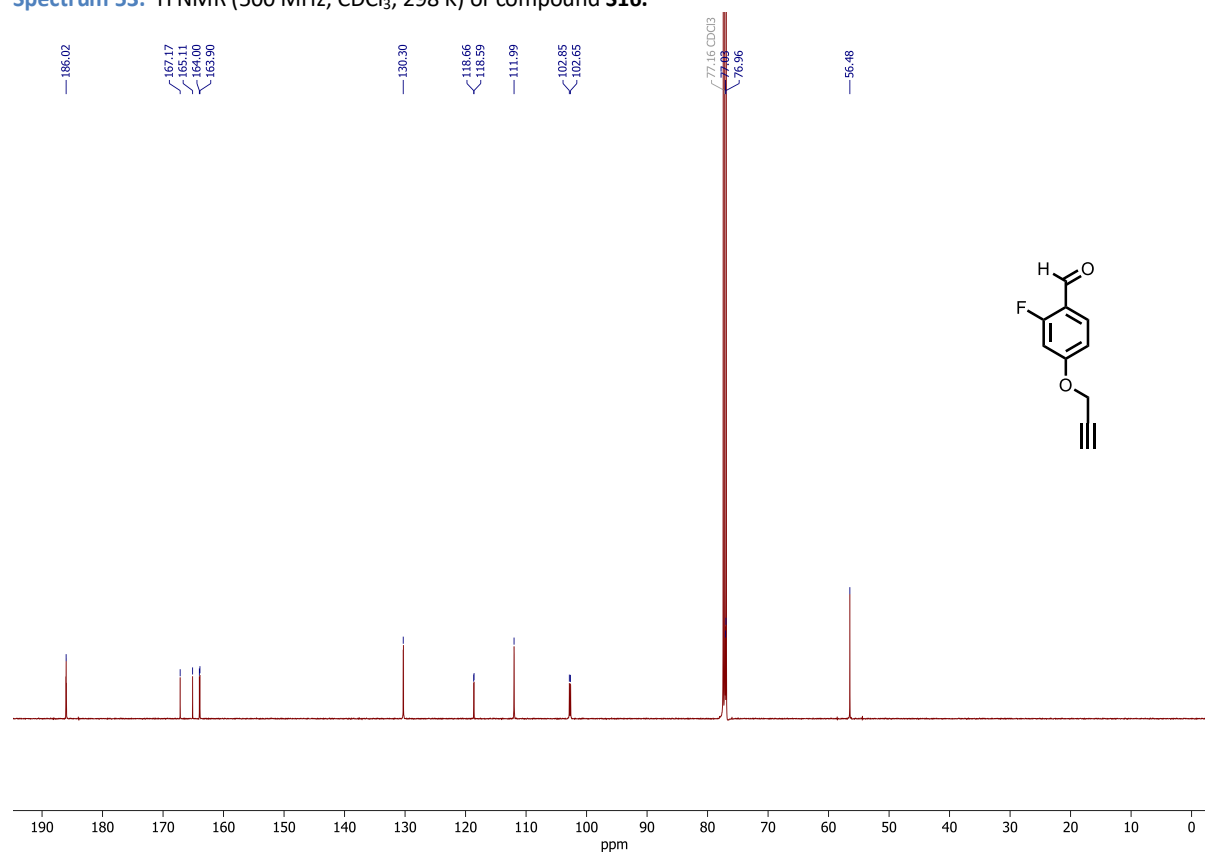
**Spectrum 50.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S15**.



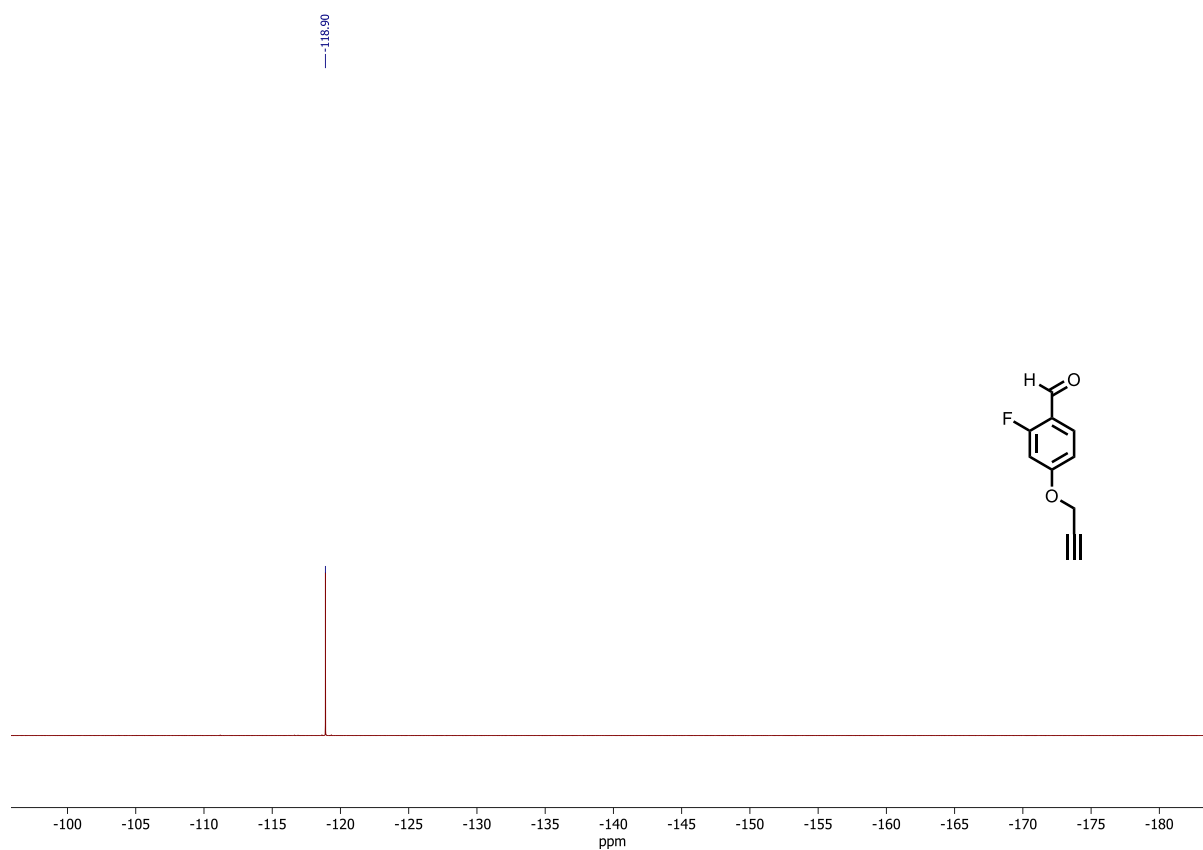
## 5.20 Spectra of S16



**Spectrum 53.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound S16.

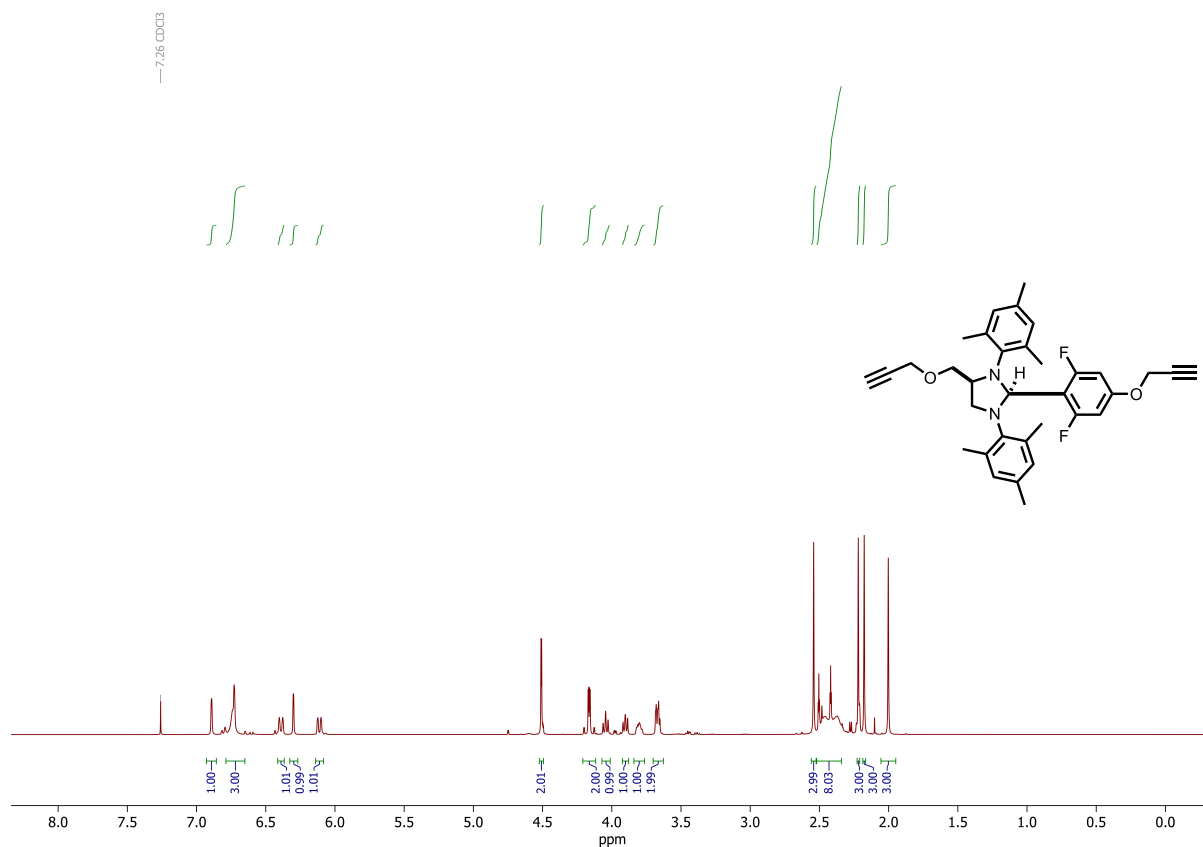


**Spectrum 54.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound S16.

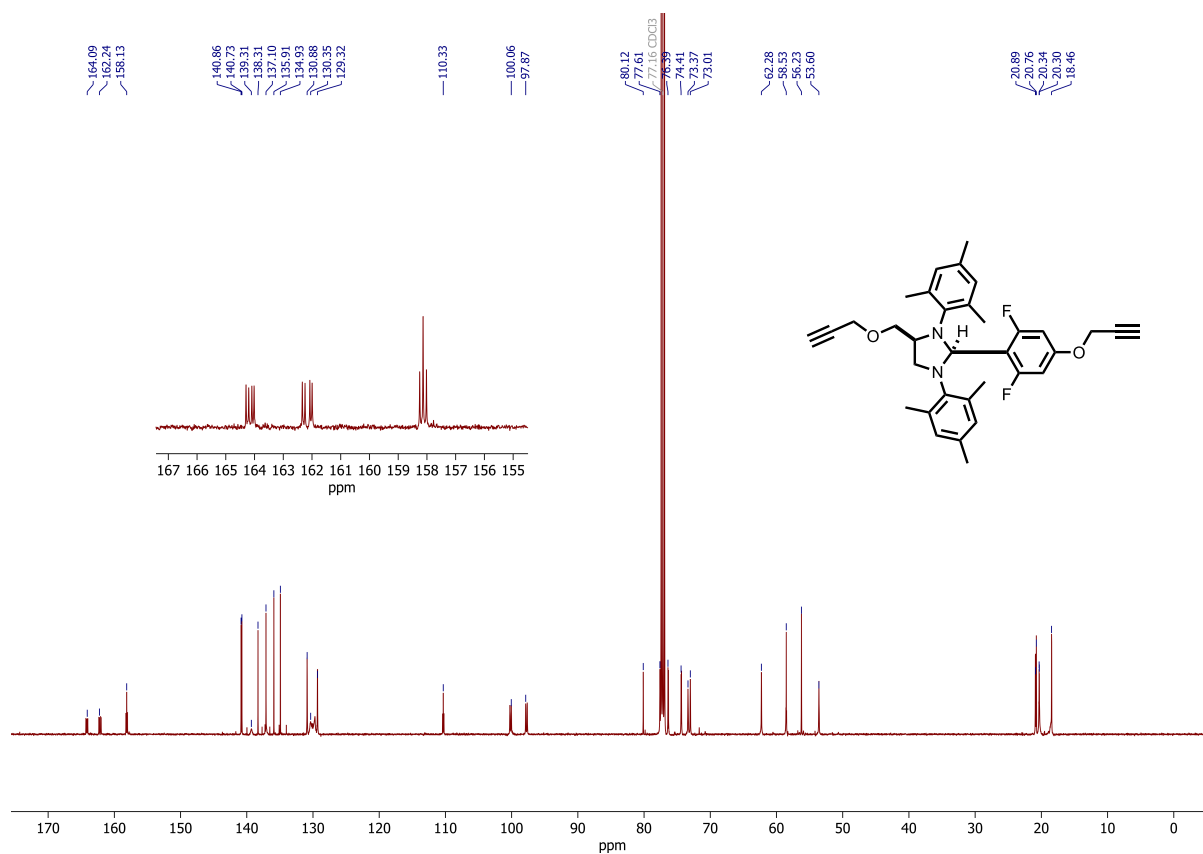


**Spectrum 55.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **S16**.

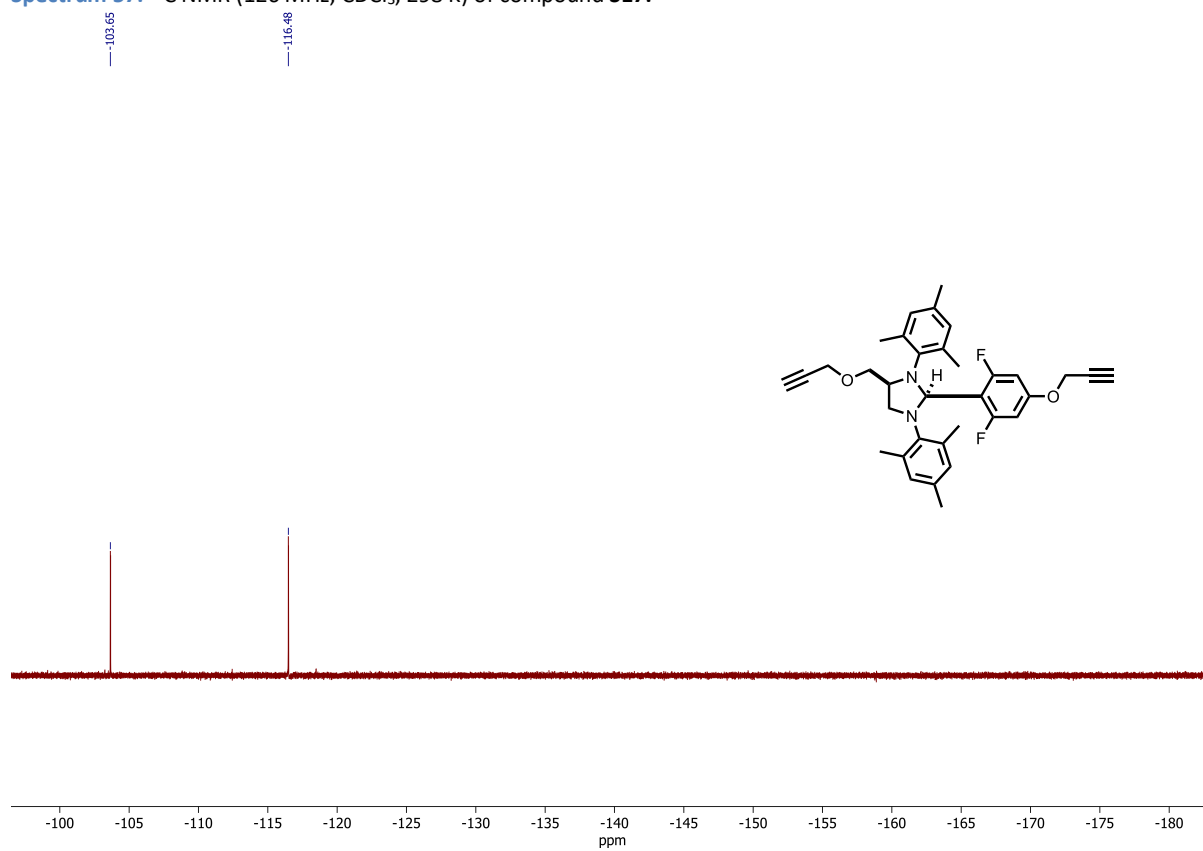
## 5.21 Spectra of S17



**Spectrum 56.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound **S17**.

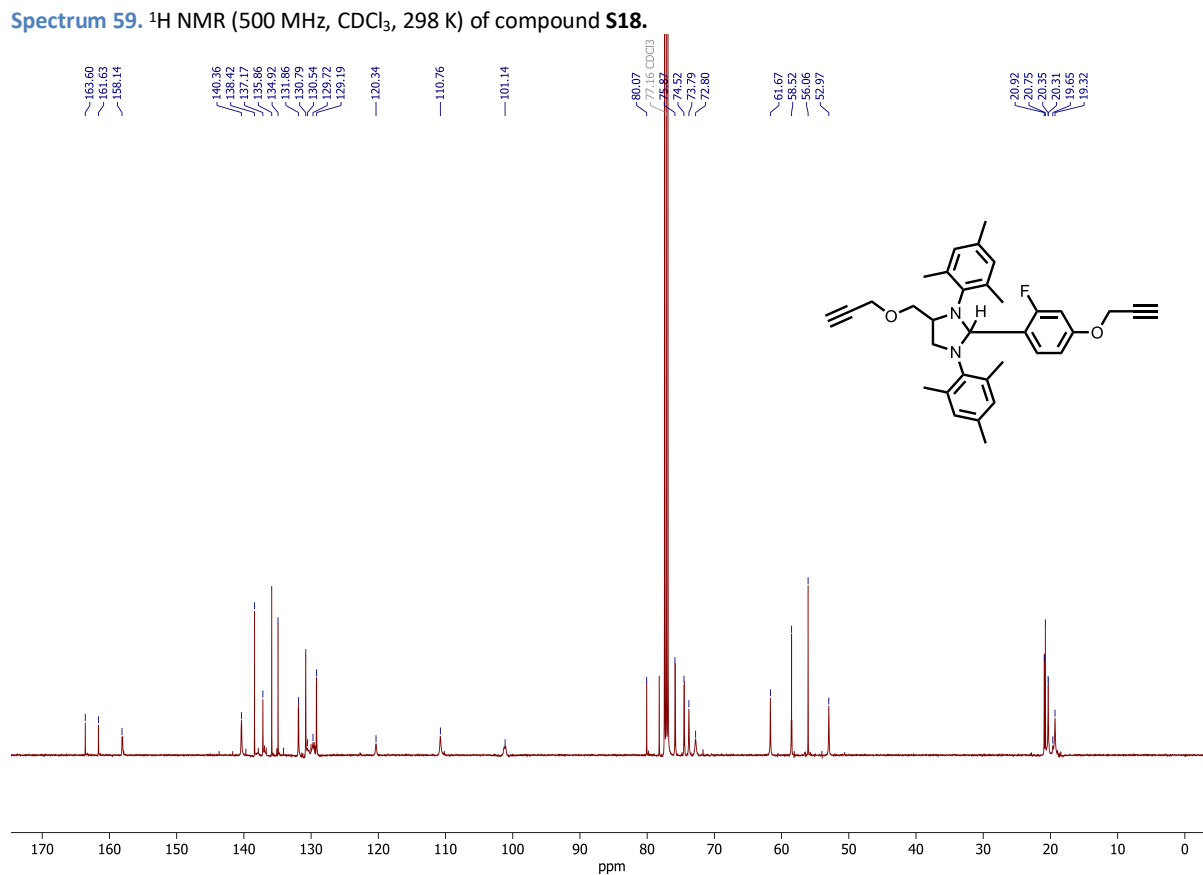
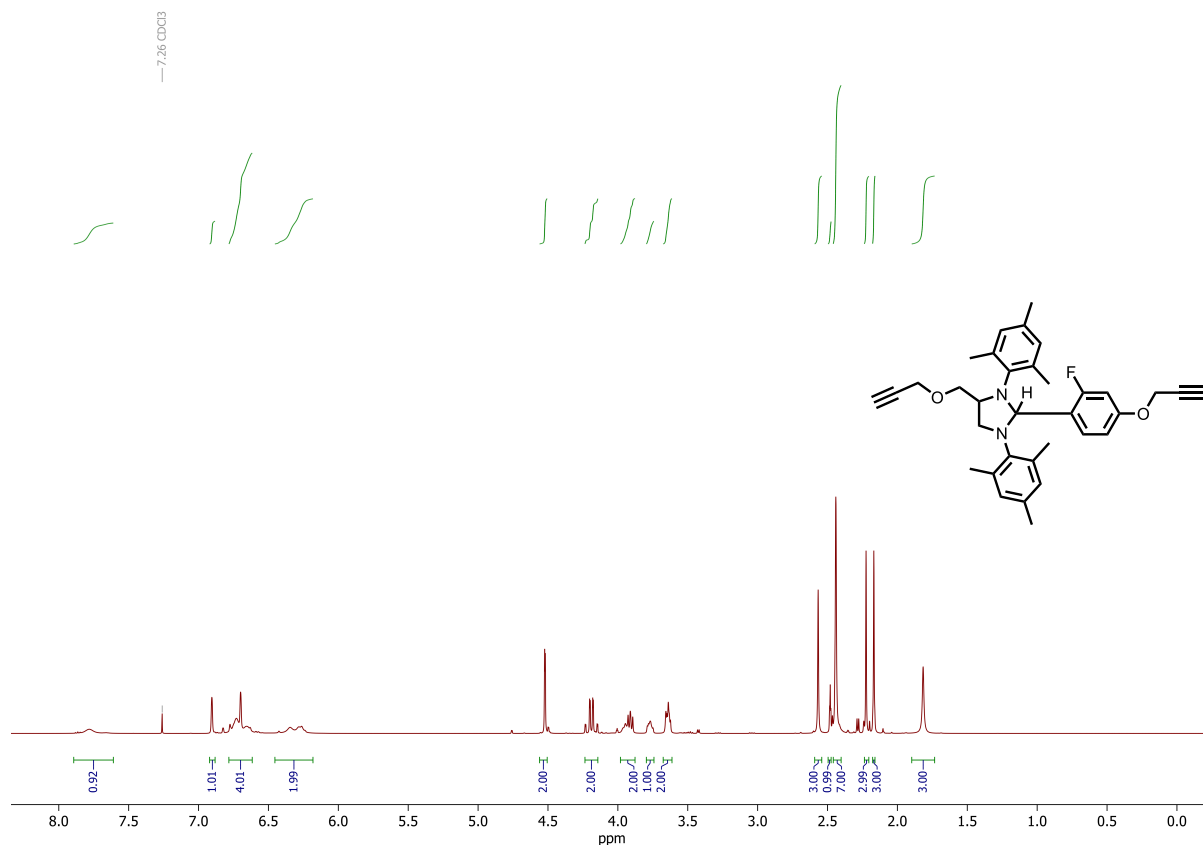


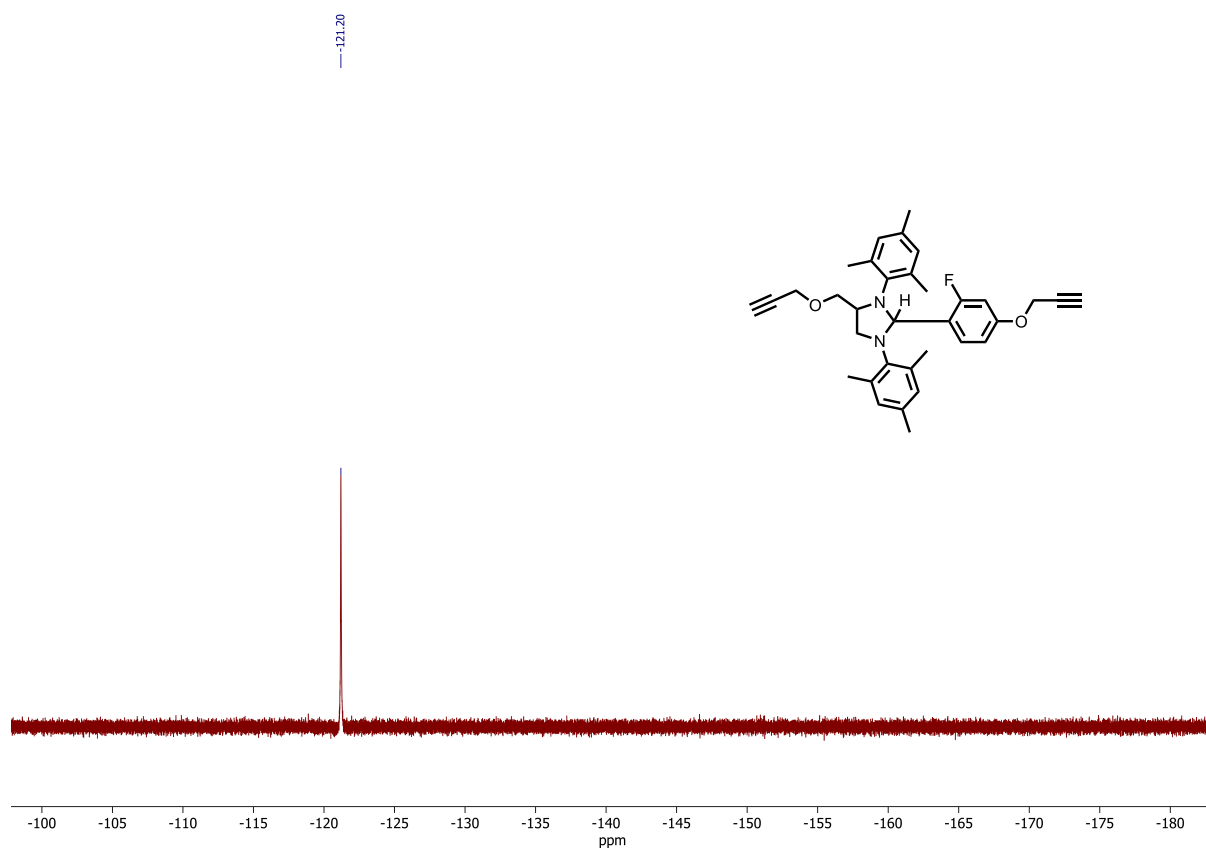
**Spectrum 57.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S17**.



**Spectrum 58.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **S17**.

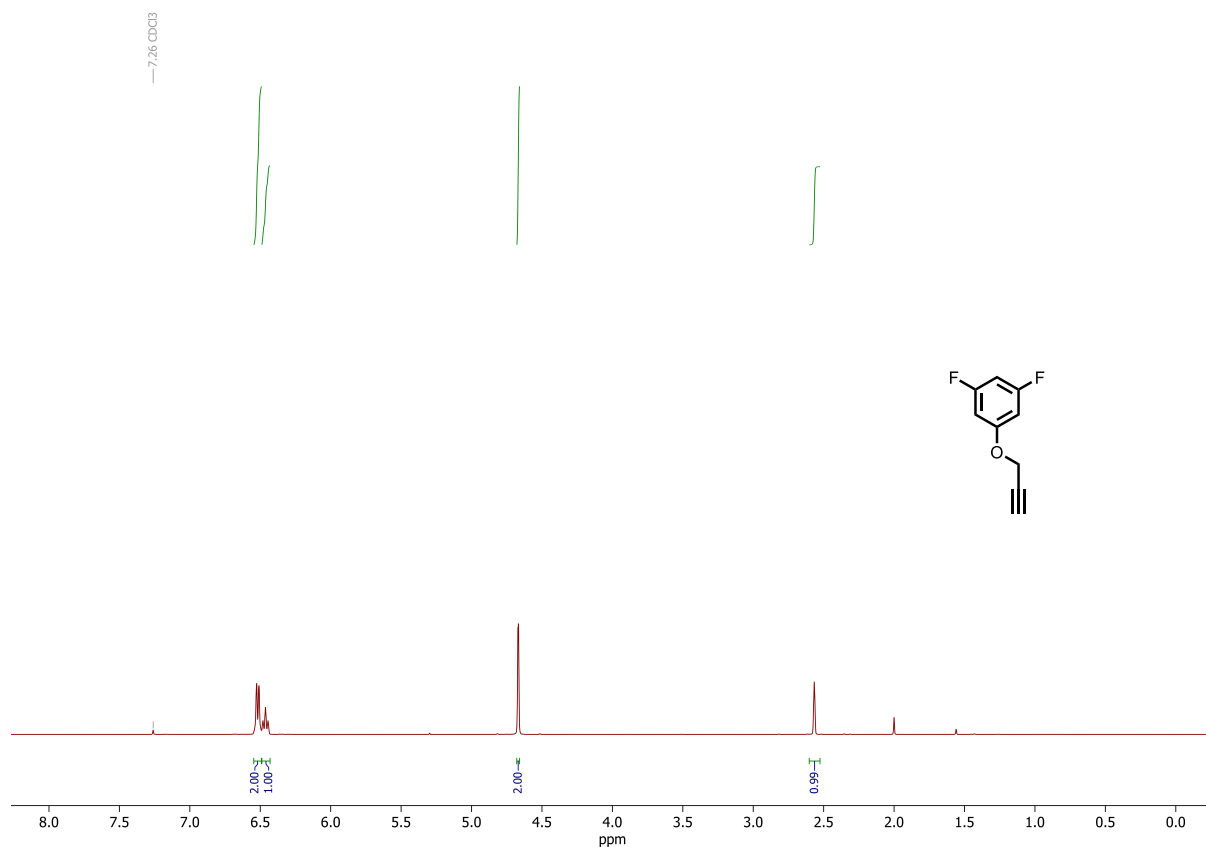
## 5.22 Spectra of S18





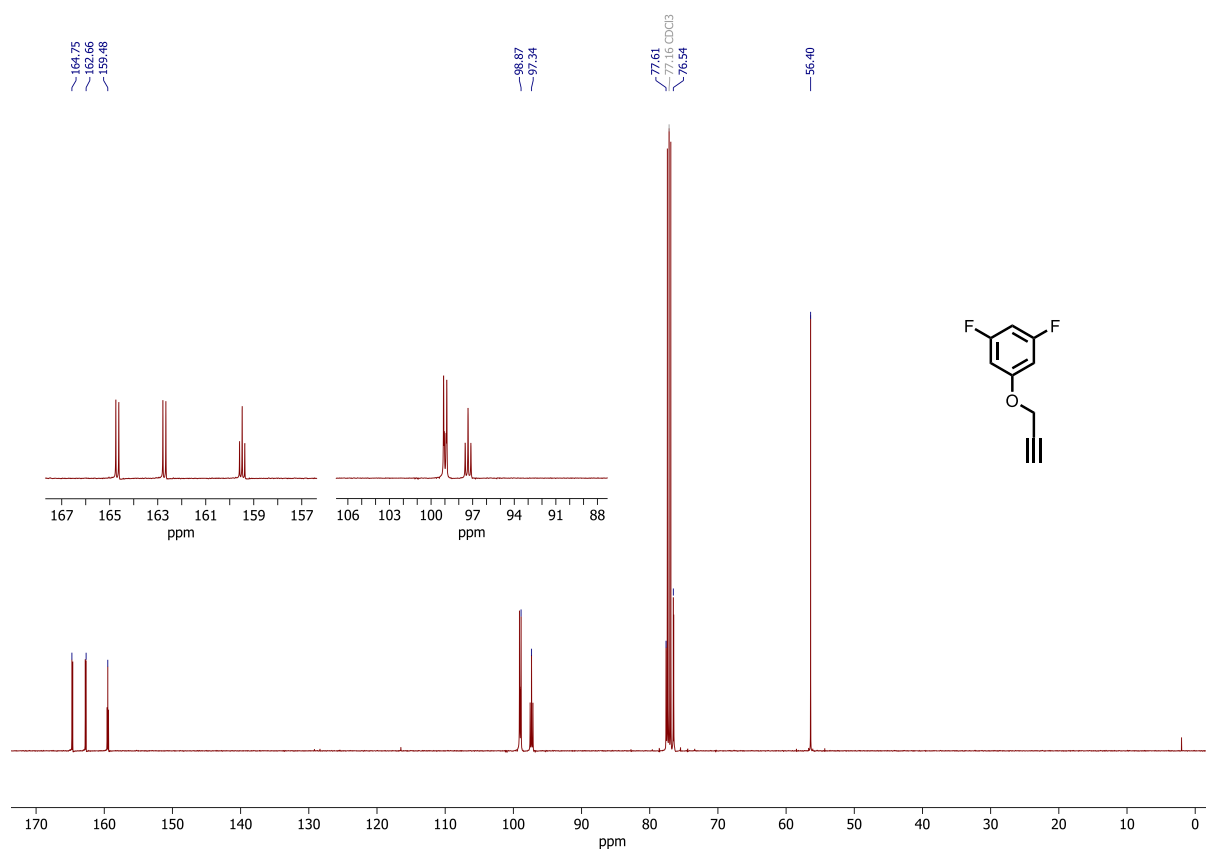
**Spectrum 61.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S18**.

## 5.23 Spectra of S19

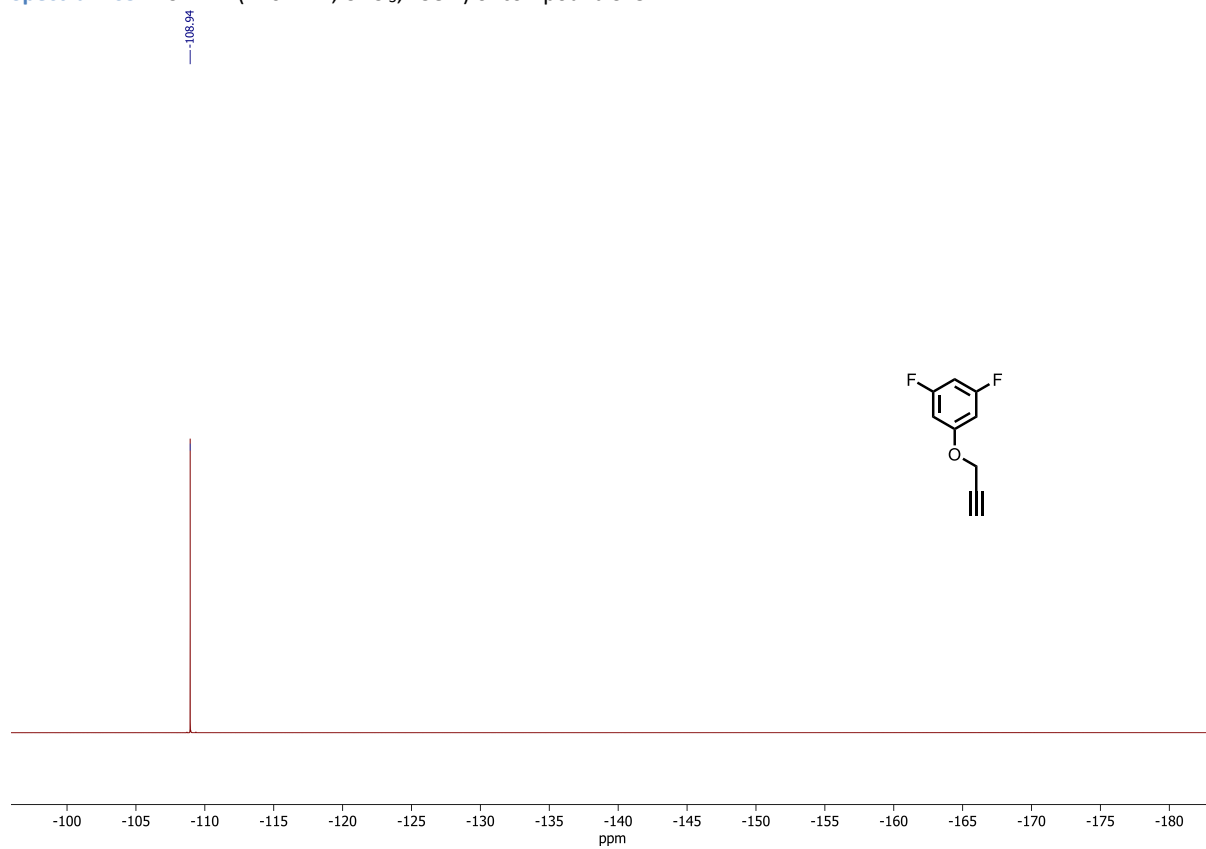


**Spectrum 62.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S19**.



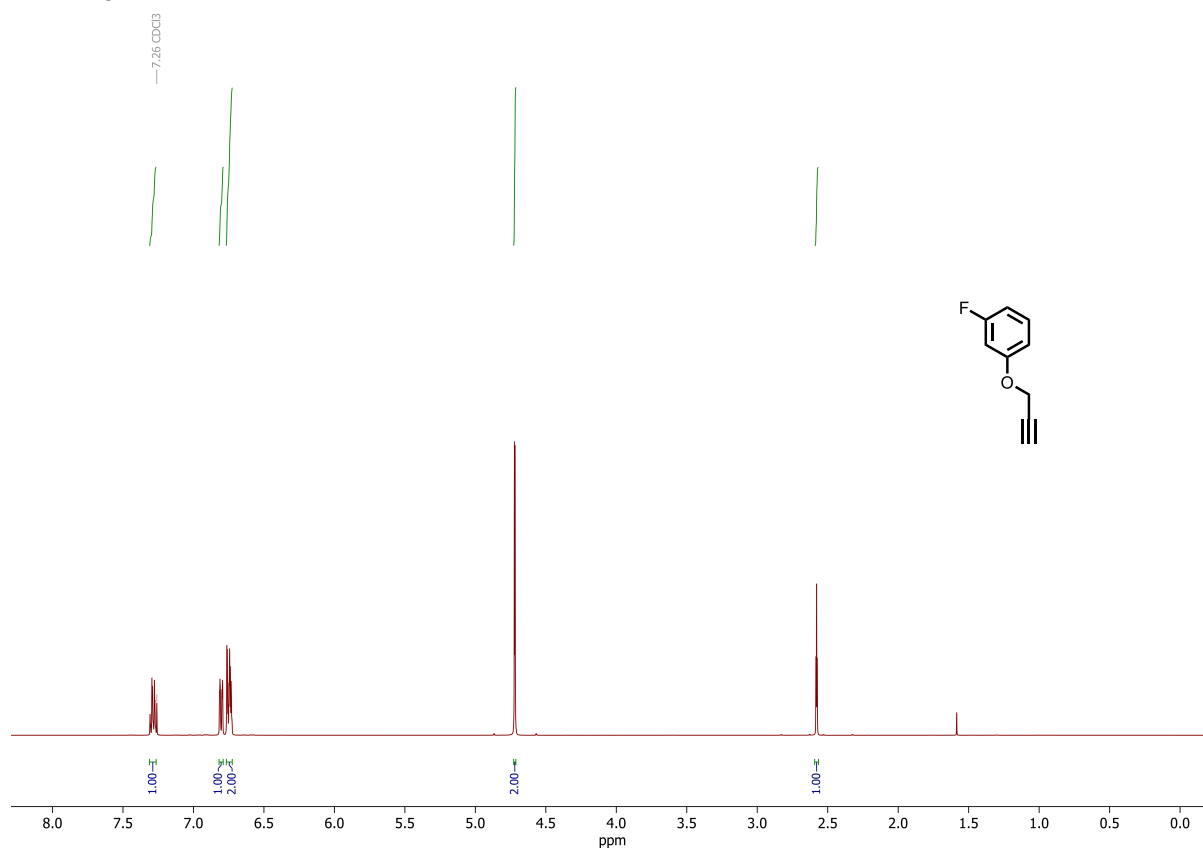


**Spectrum 63.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound **S19**.

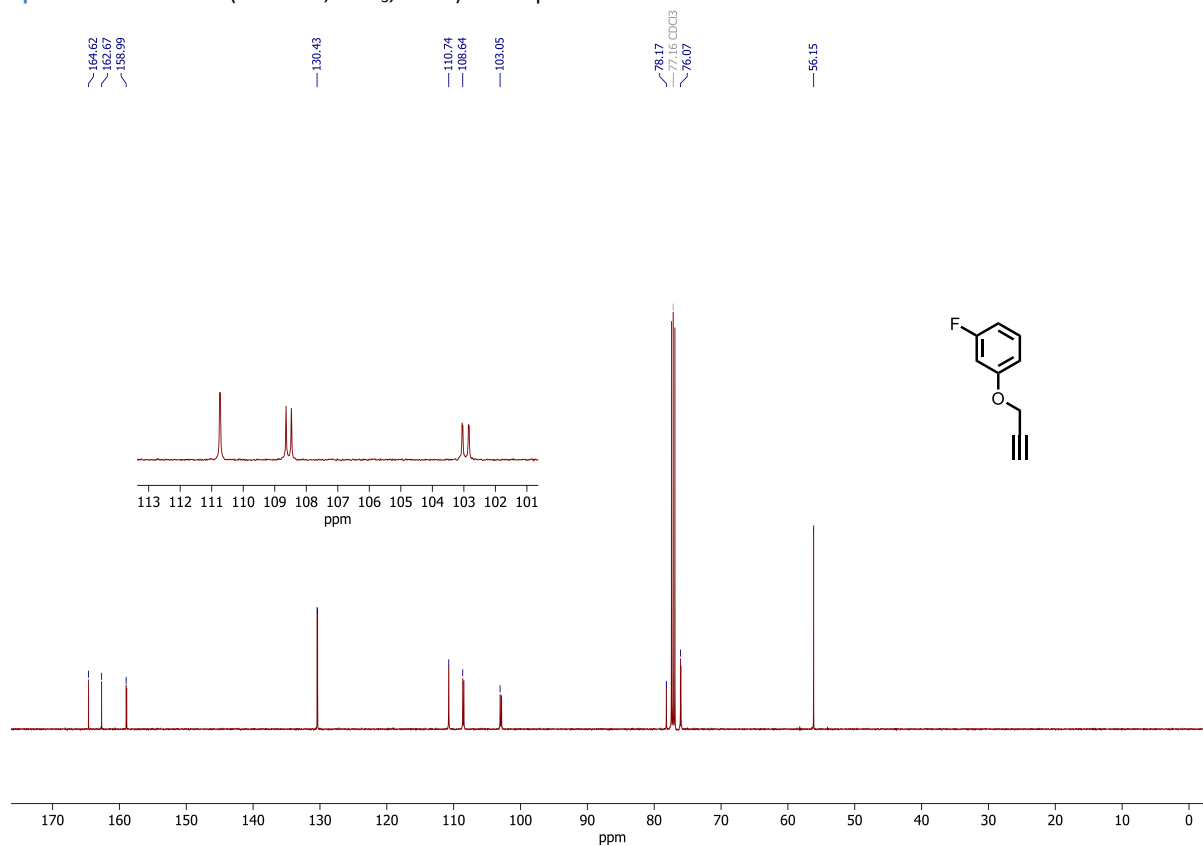


**Spectrum 64.** <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) of compound **S19**.

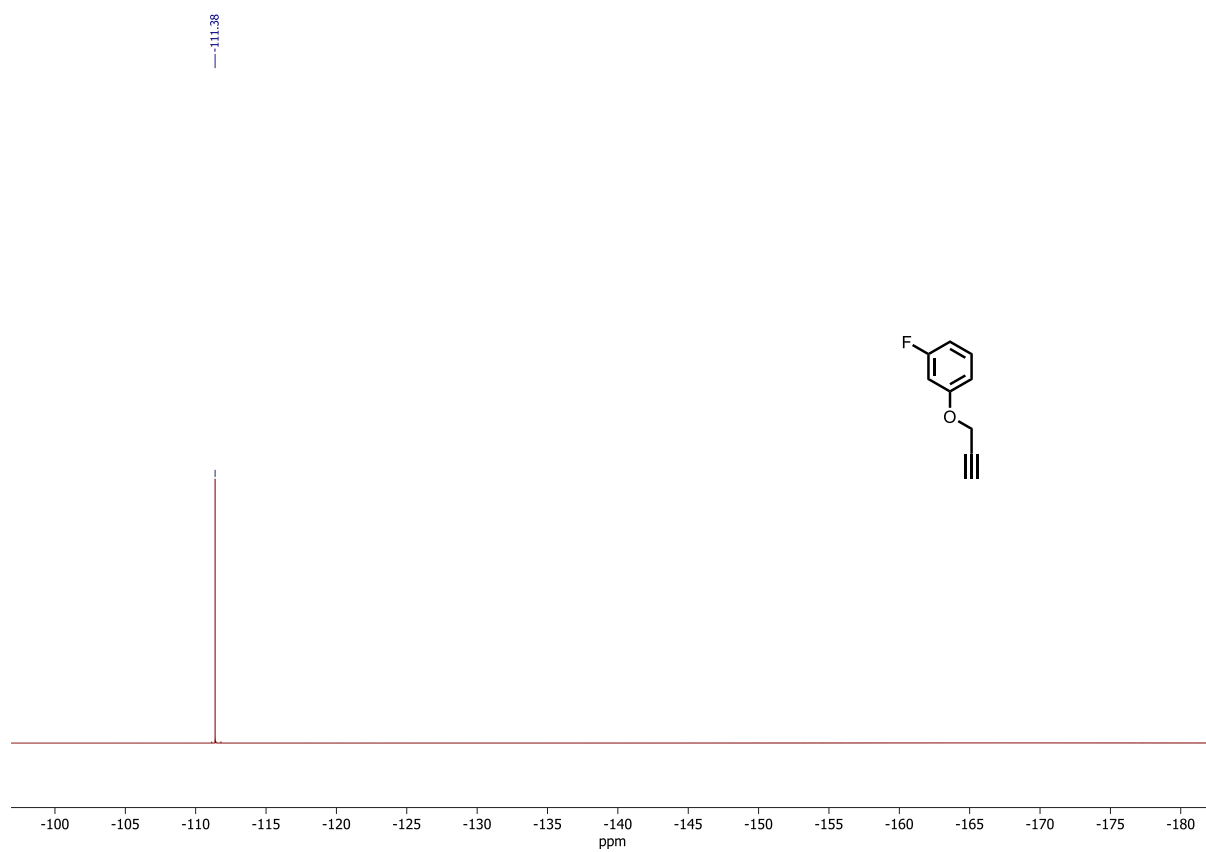
## 5.24 Spectra of S20



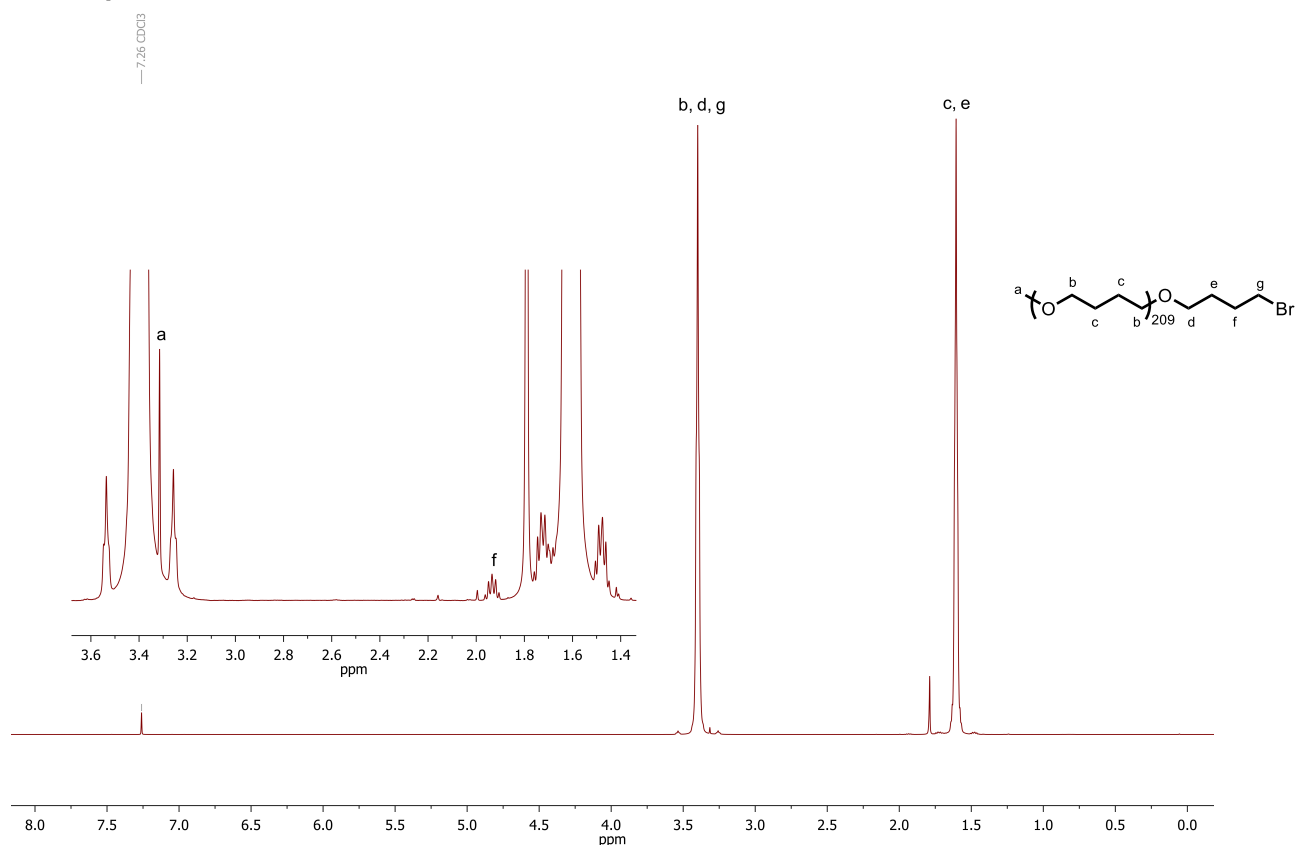
**Spectrum 65.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of compound S20.



**Spectrum 66.** <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 298 K) of compound S20.

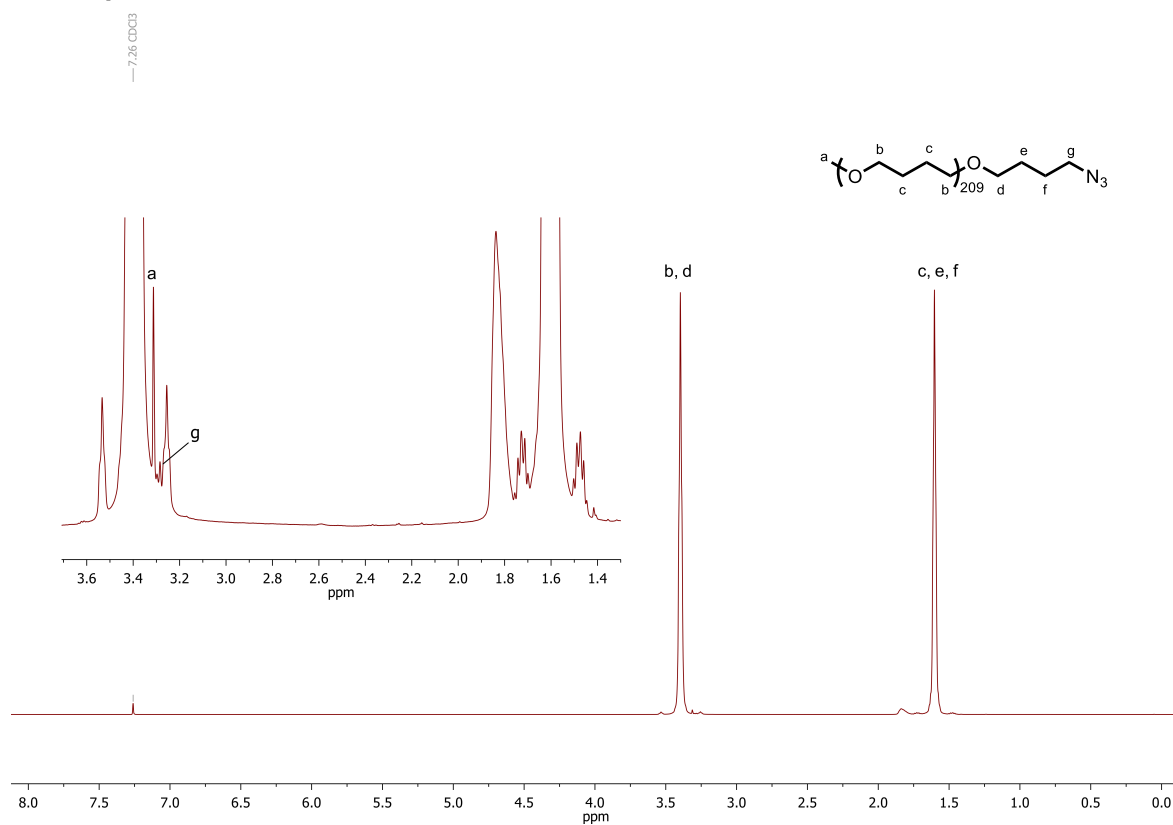


## 5.25 Spectrum of S21



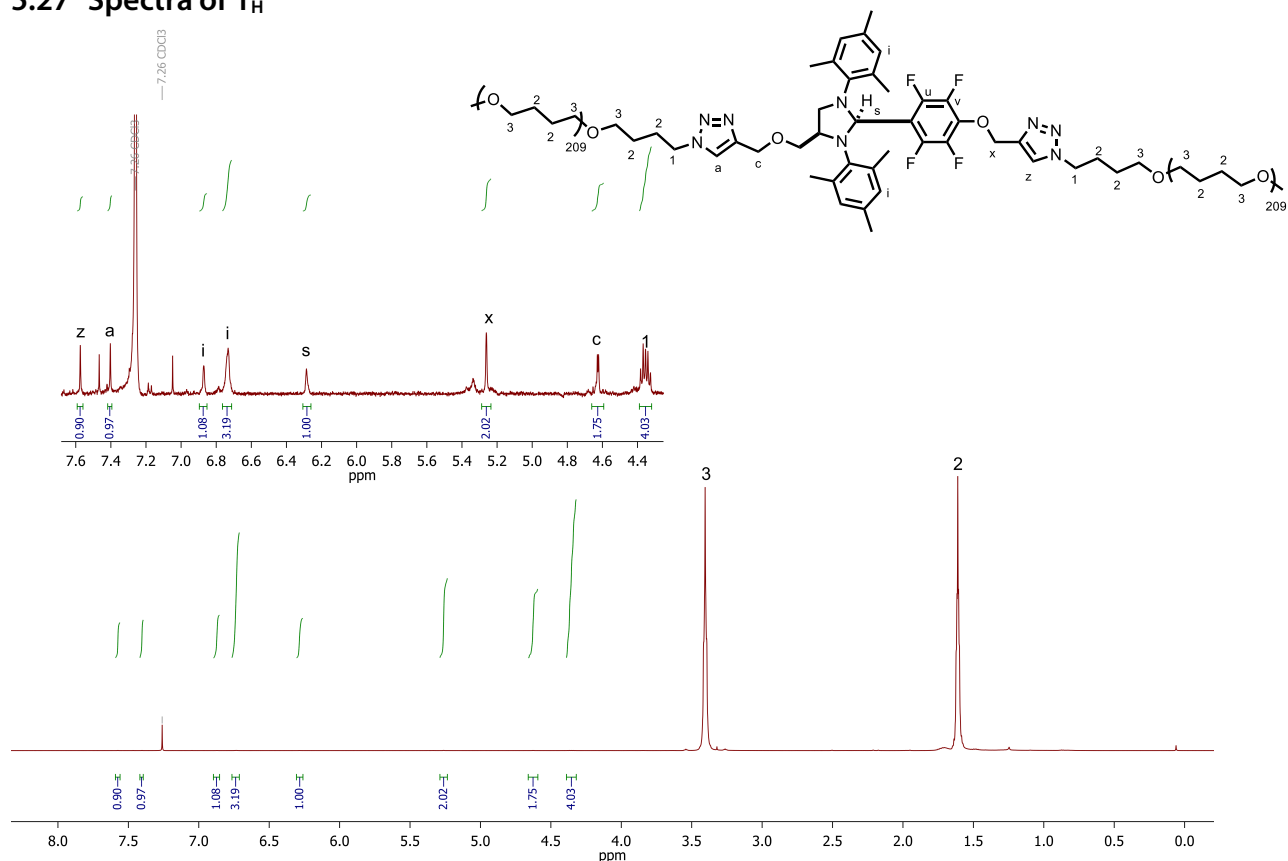
**Spectrum 68.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of compound **S21**.

## 5.26 Spectrum of 3

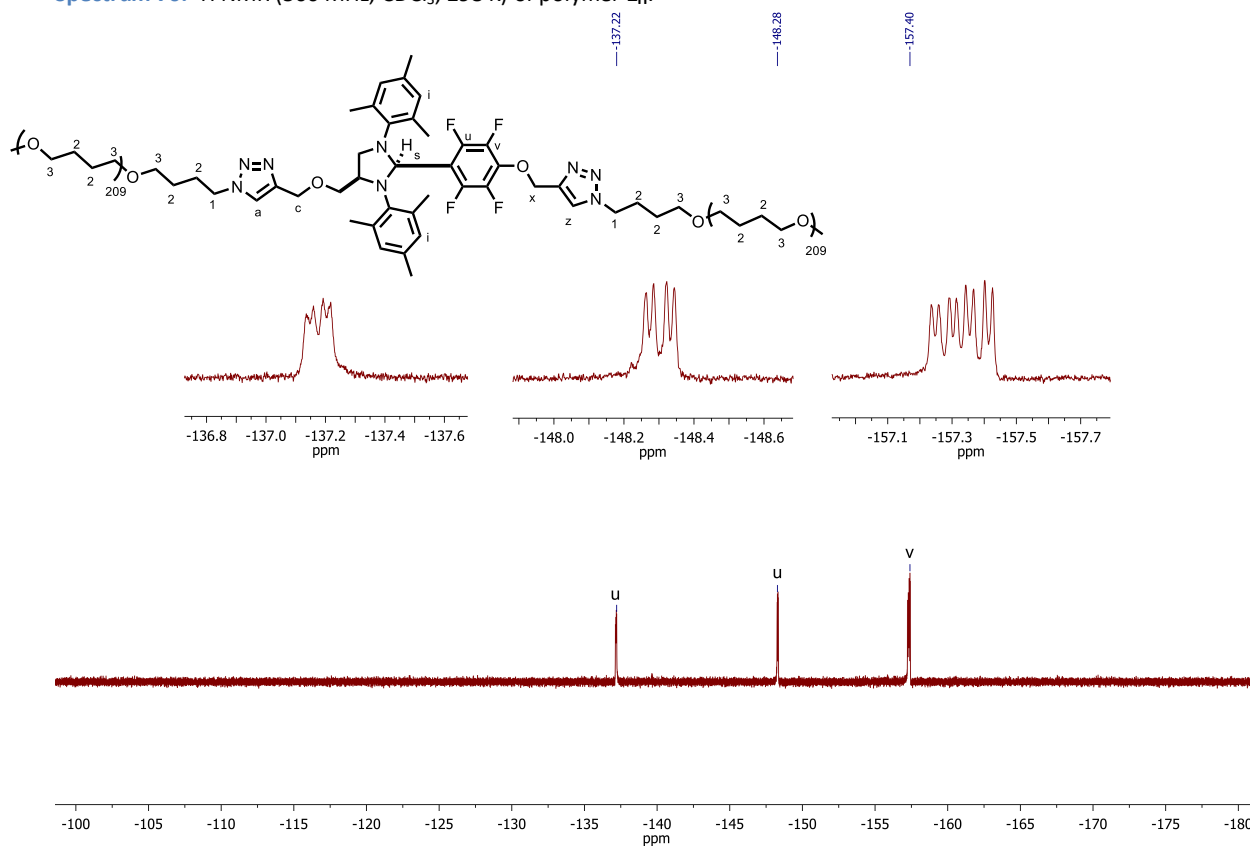


**Spectrum 69.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of compound **3**.

## 5.27 Spectra of $1_H$

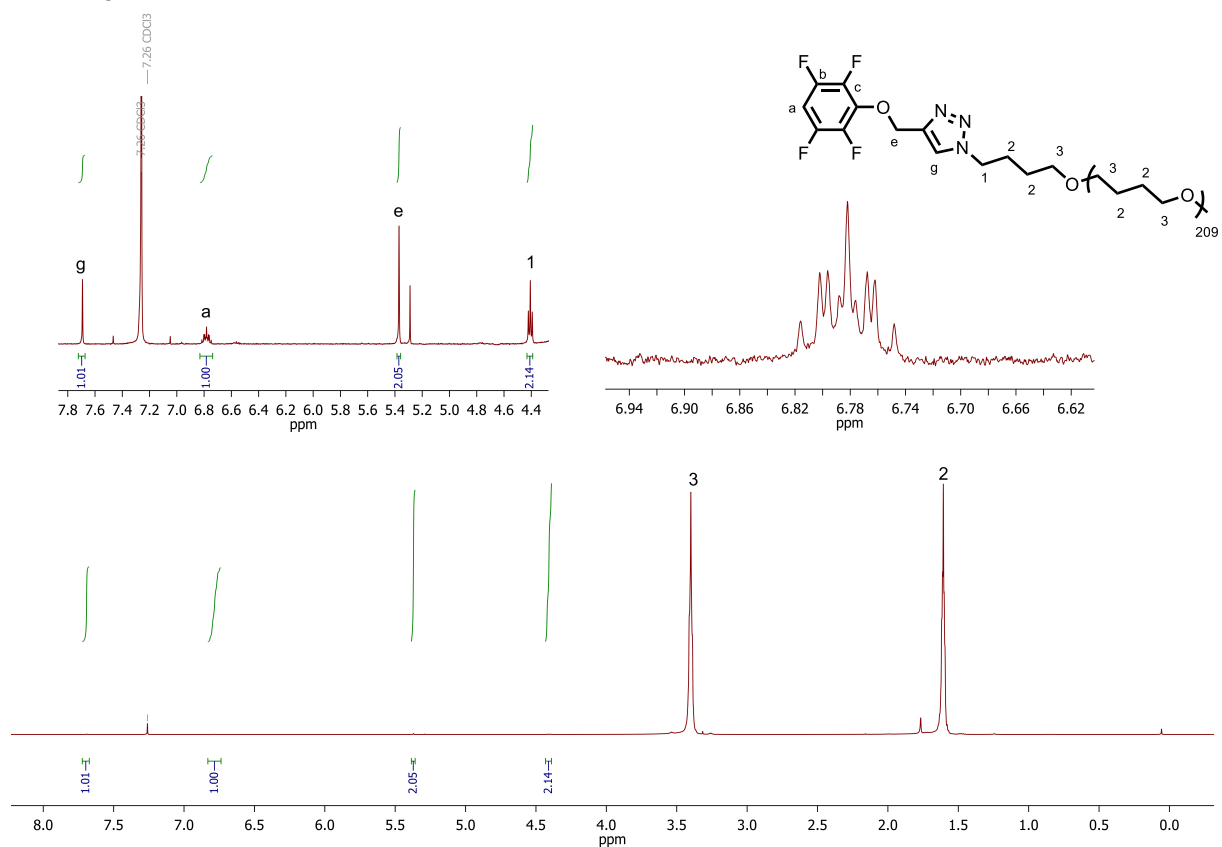


**Spectrum 70.**  $1_H$  NMR (500 MHz,  $CDCl_3$ , 298 K) of polymer  $1_H$ .

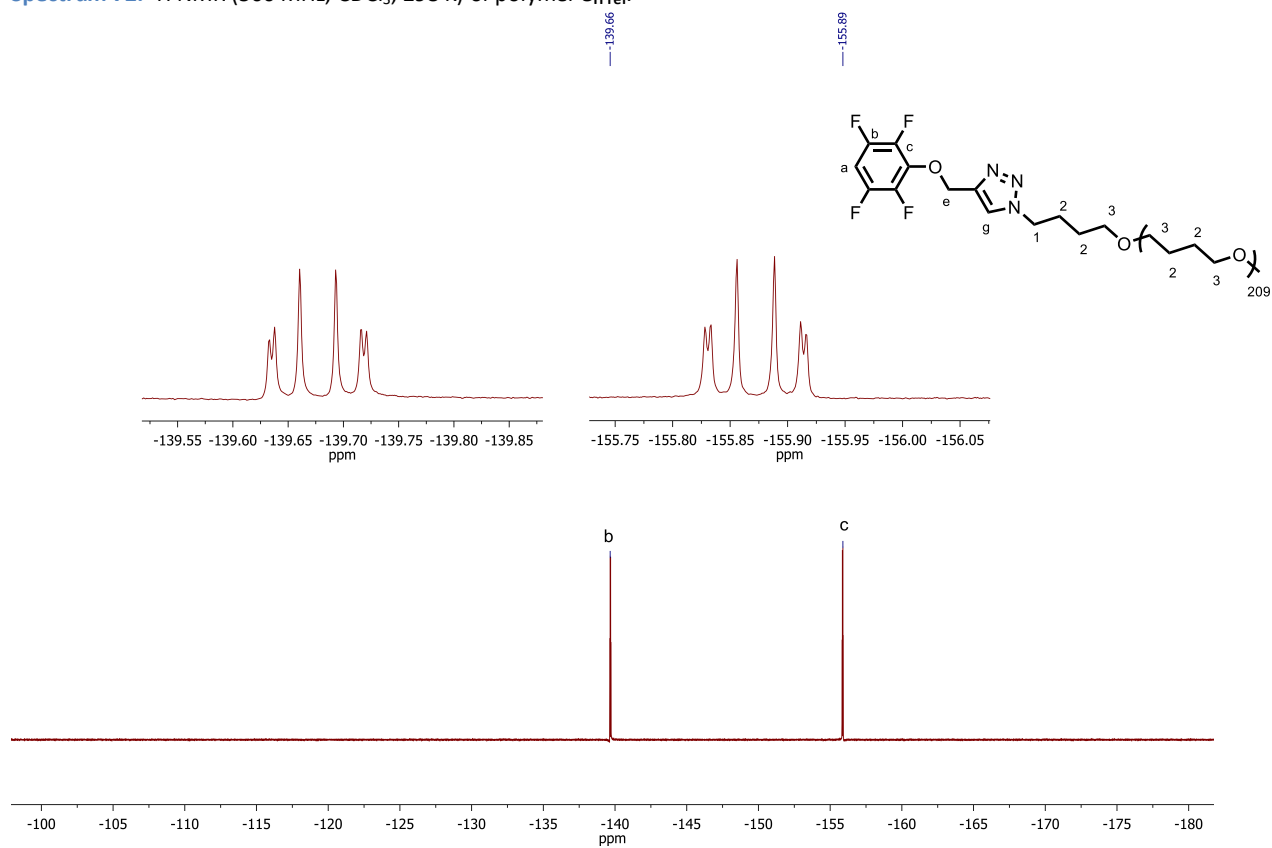


**Spectrum 71.**  $^{19}F$  NMR (376 MHz,  $CDCl_3$ , 298 K) of polymer  $1_H$ .

## 5.28 Spectra of 5<sub>H</sub> ref

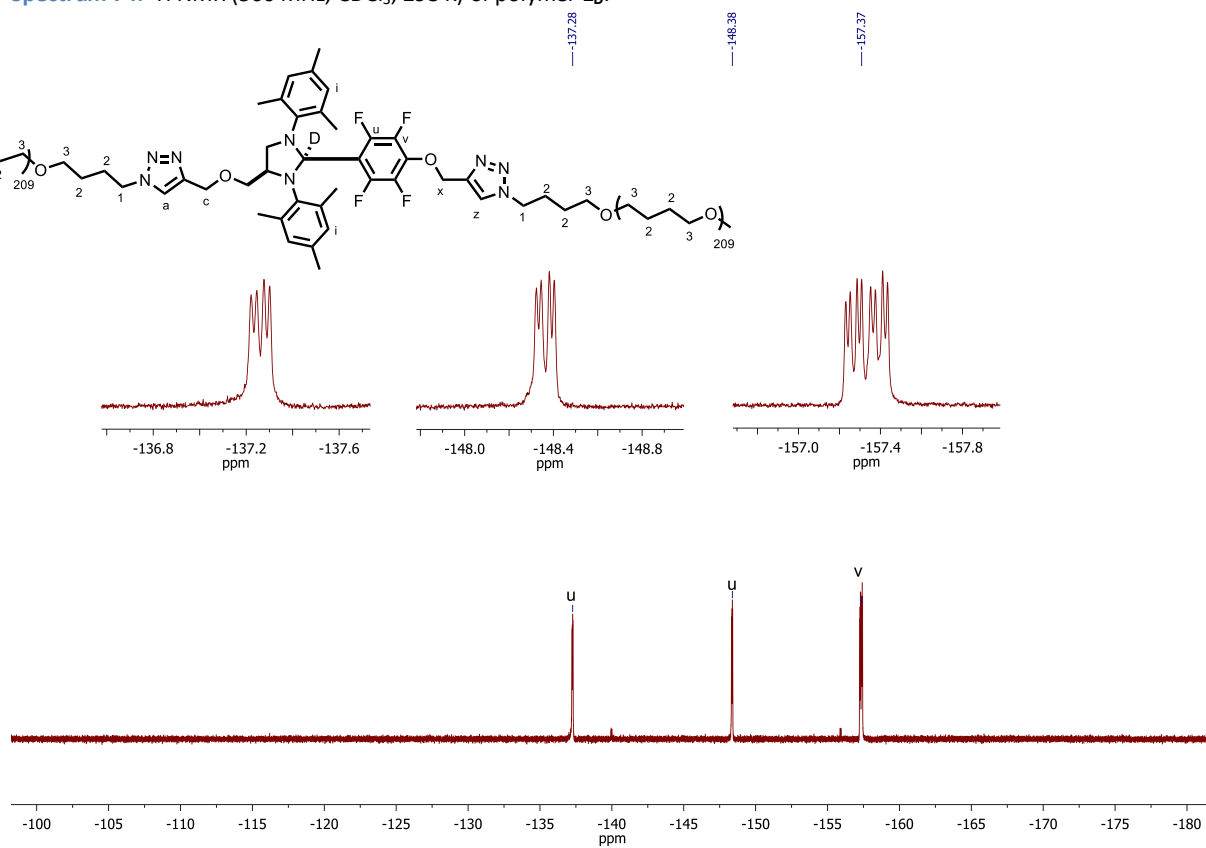
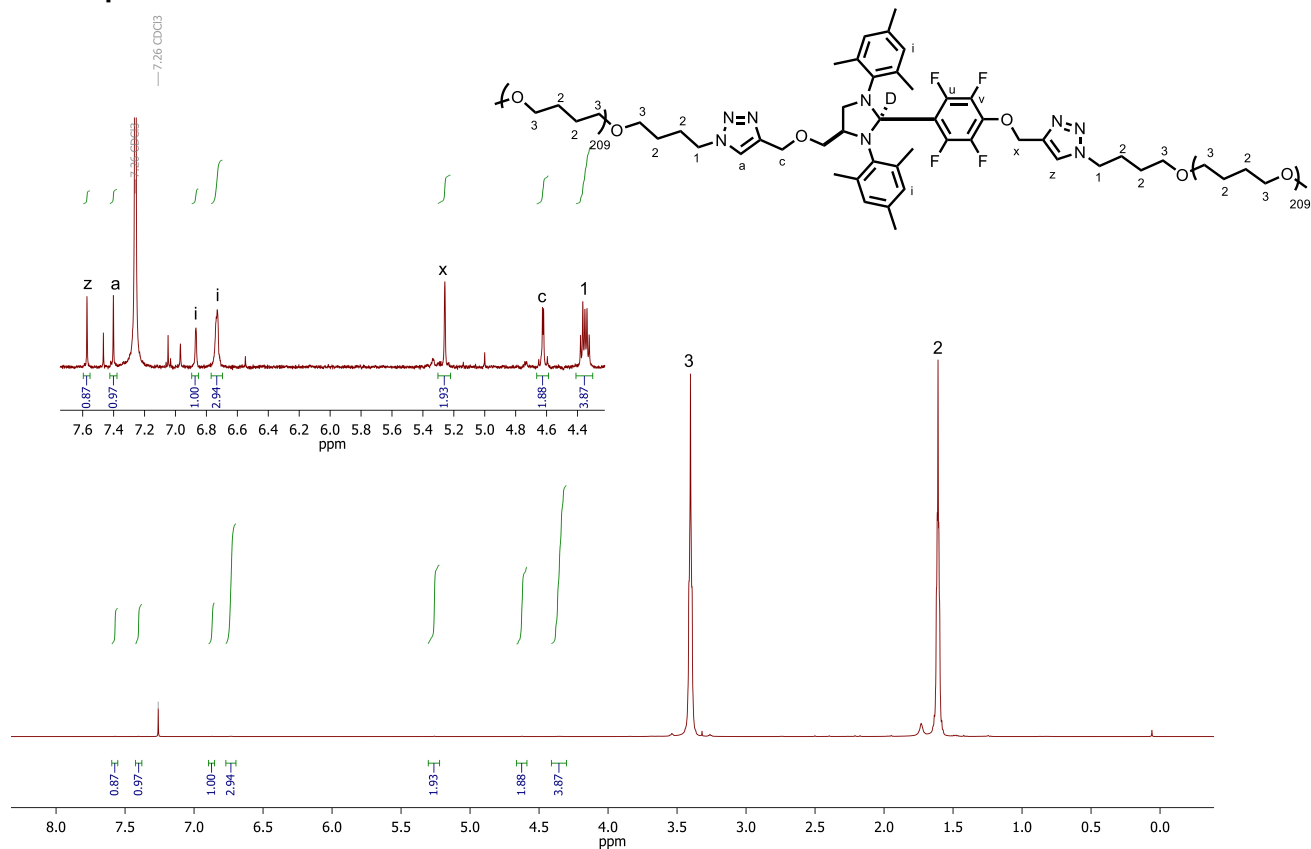


**Spectrum 72.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of polymer 5<sub>H</sub> ref.

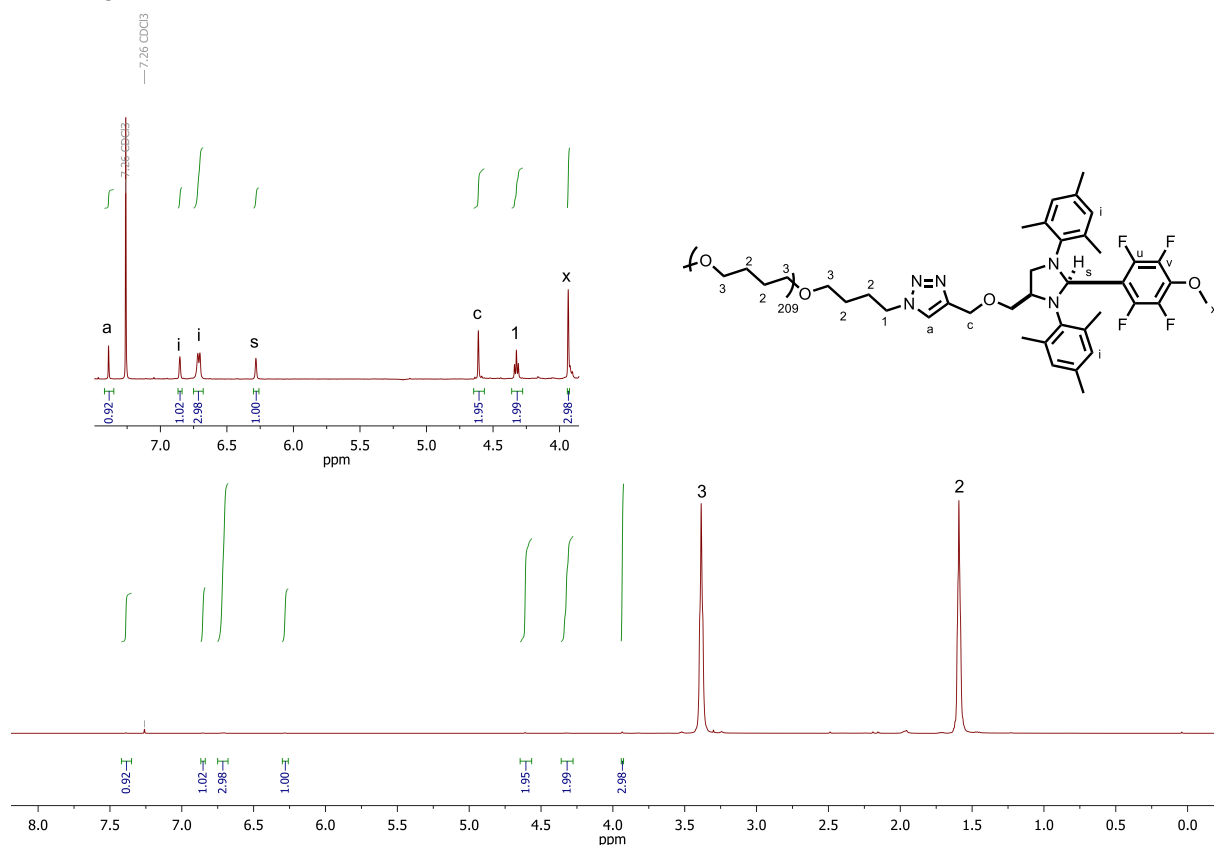


**Spectrum 73.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 298 K) of polymer 5<sub>H</sub> ref.

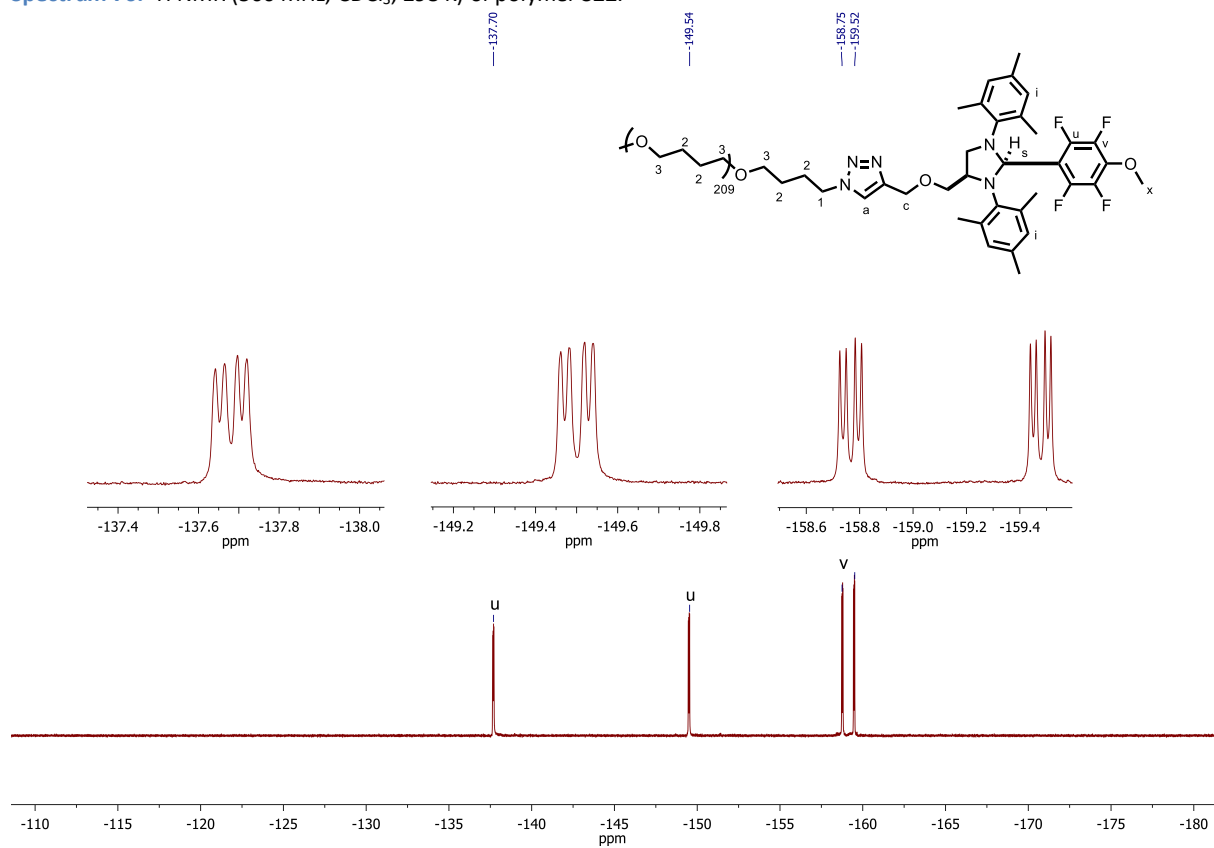
## 5.29 Spectra of 1<sub>D</sub>



### 5.30 Spectra of S22



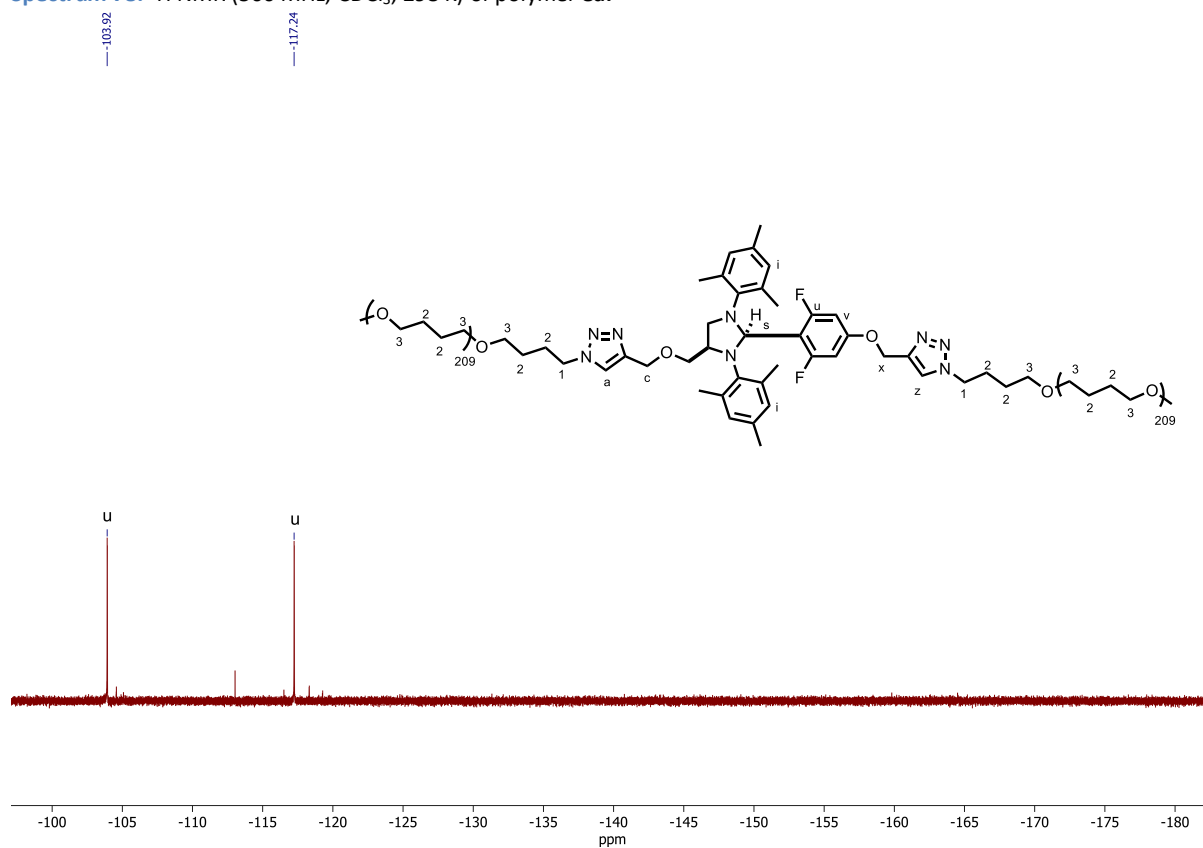
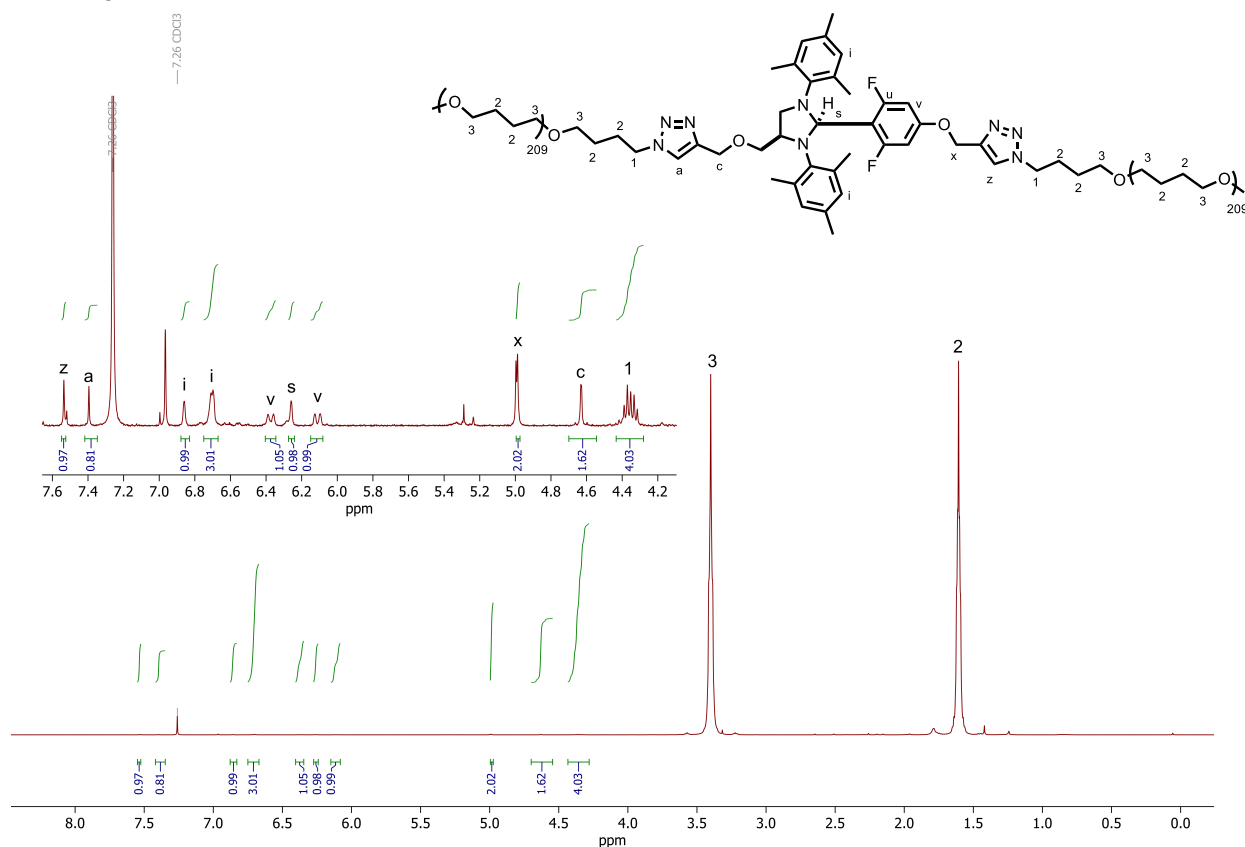
**Spectrum 76.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of polymer **S22**.



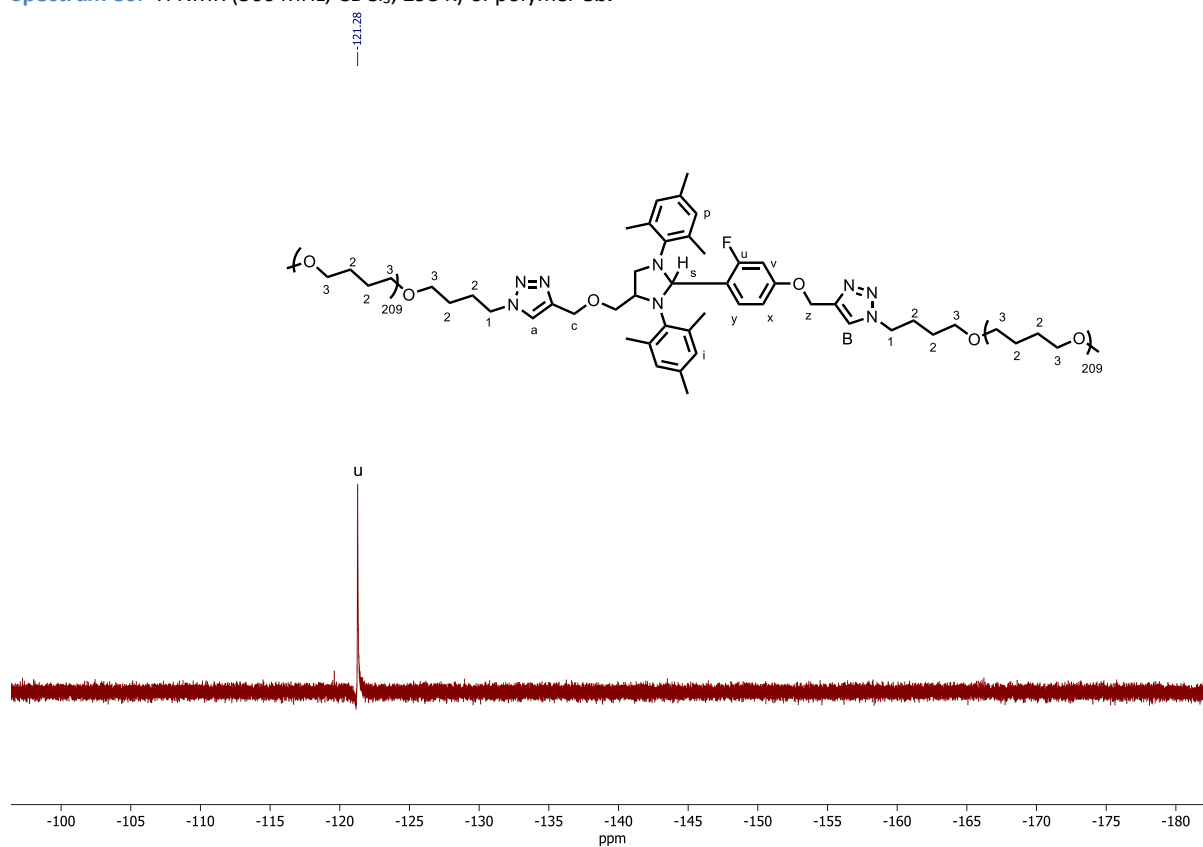
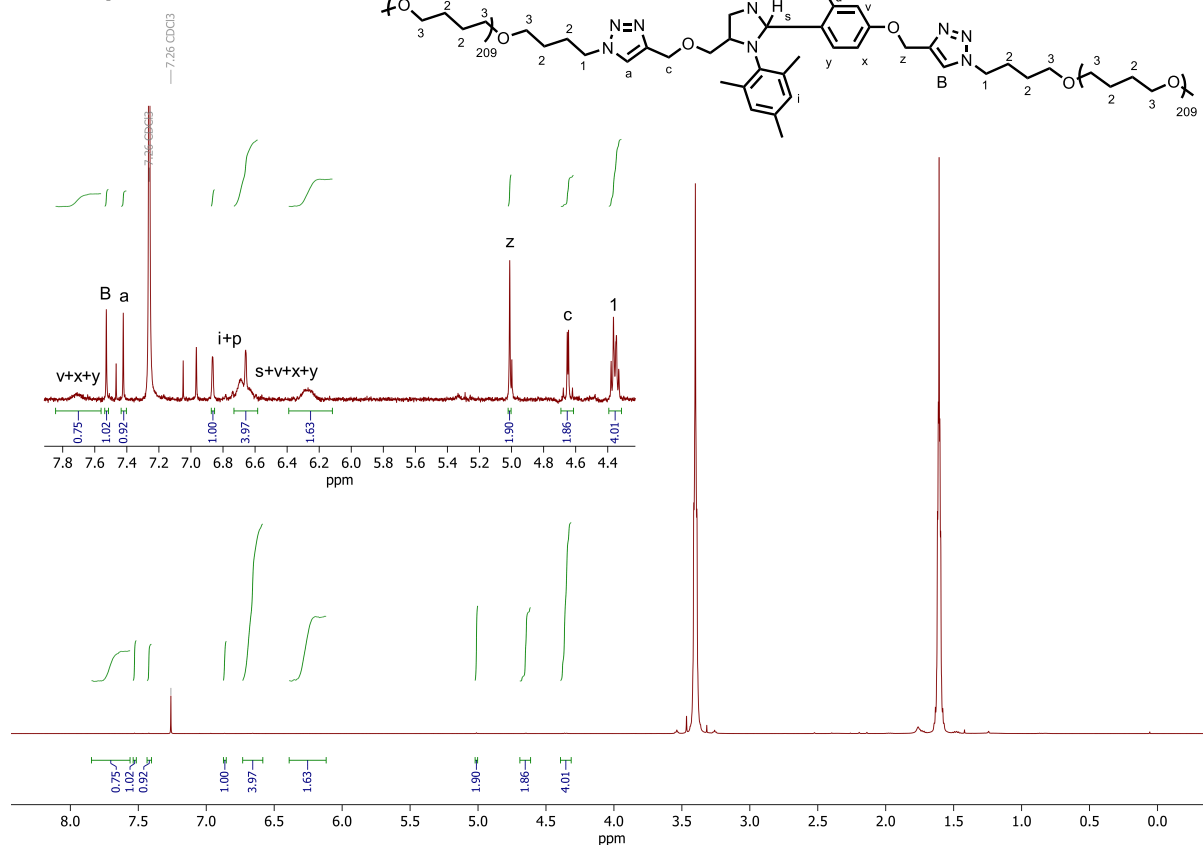
**Spectrum 77.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of polymer **S22**.



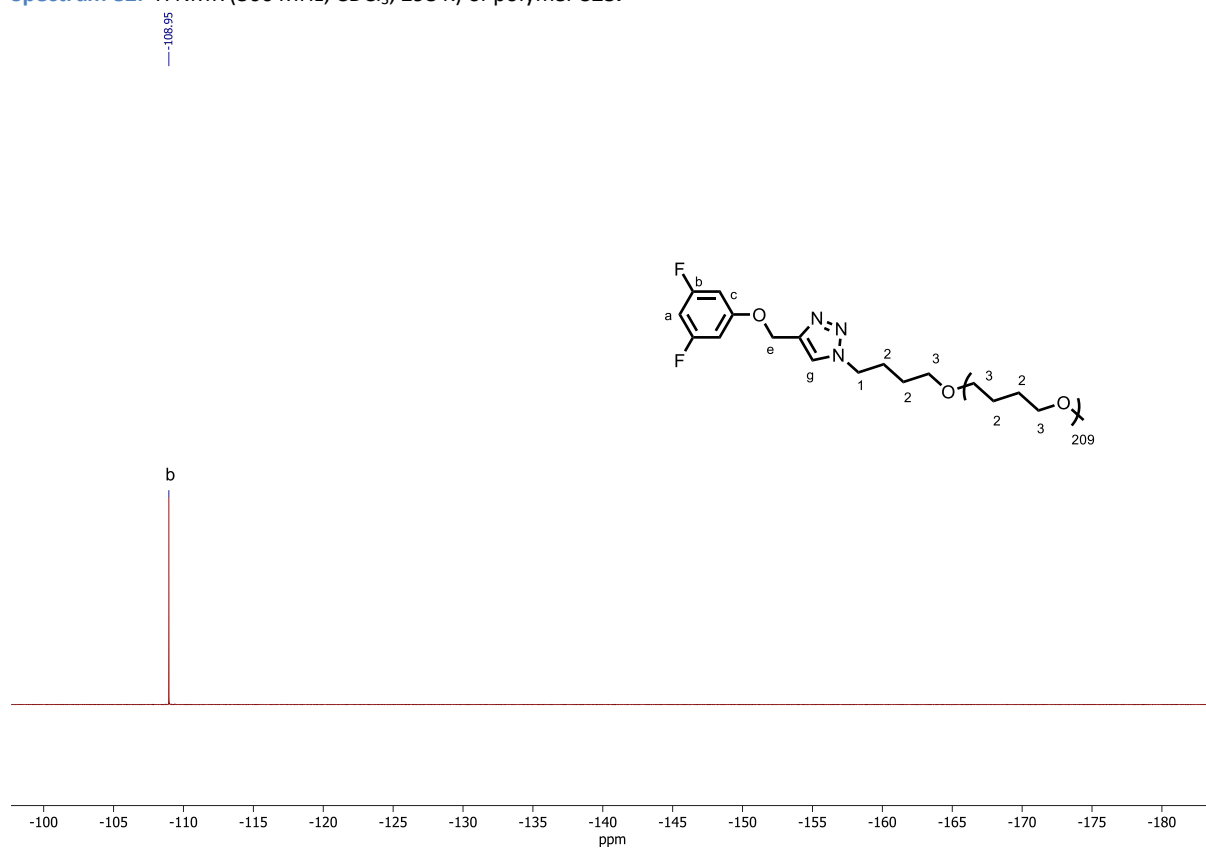
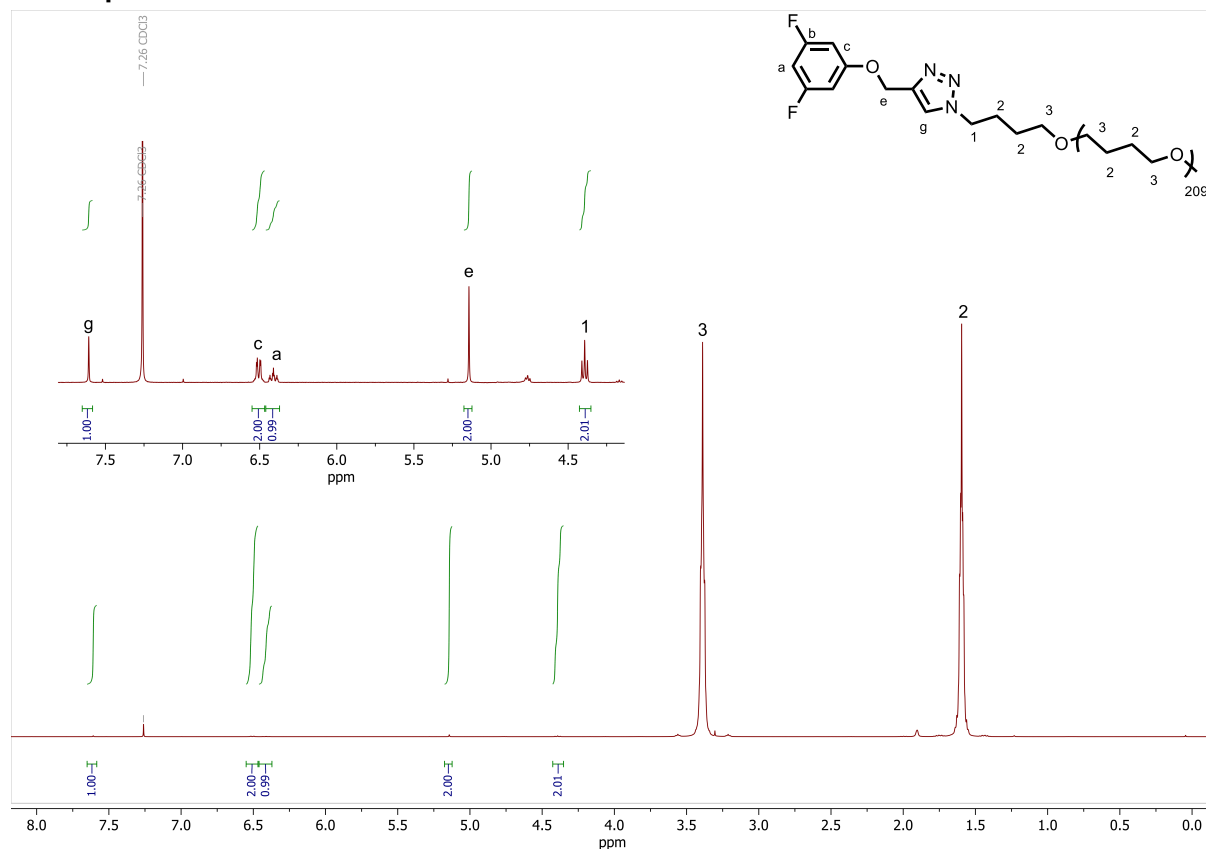
### 5.31 Spectra of 8a



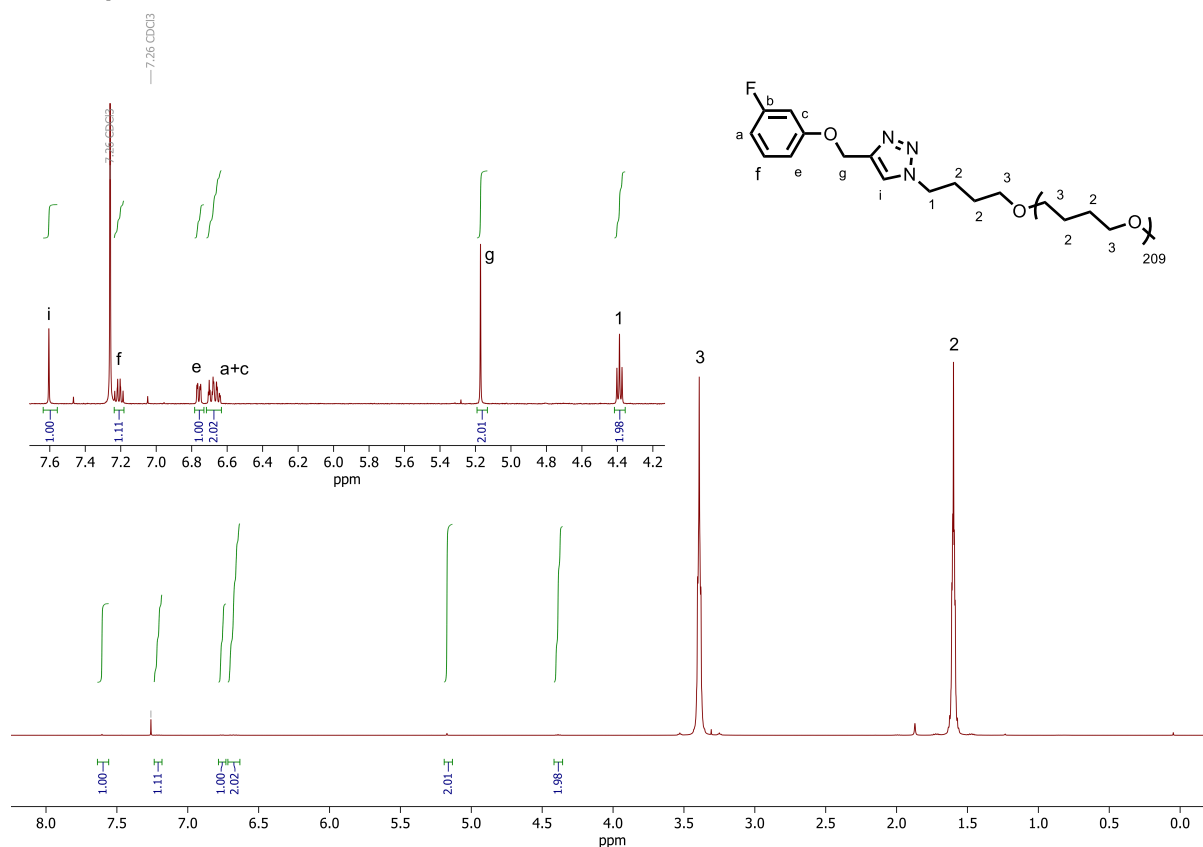
### 5.32 Spectra of 8b



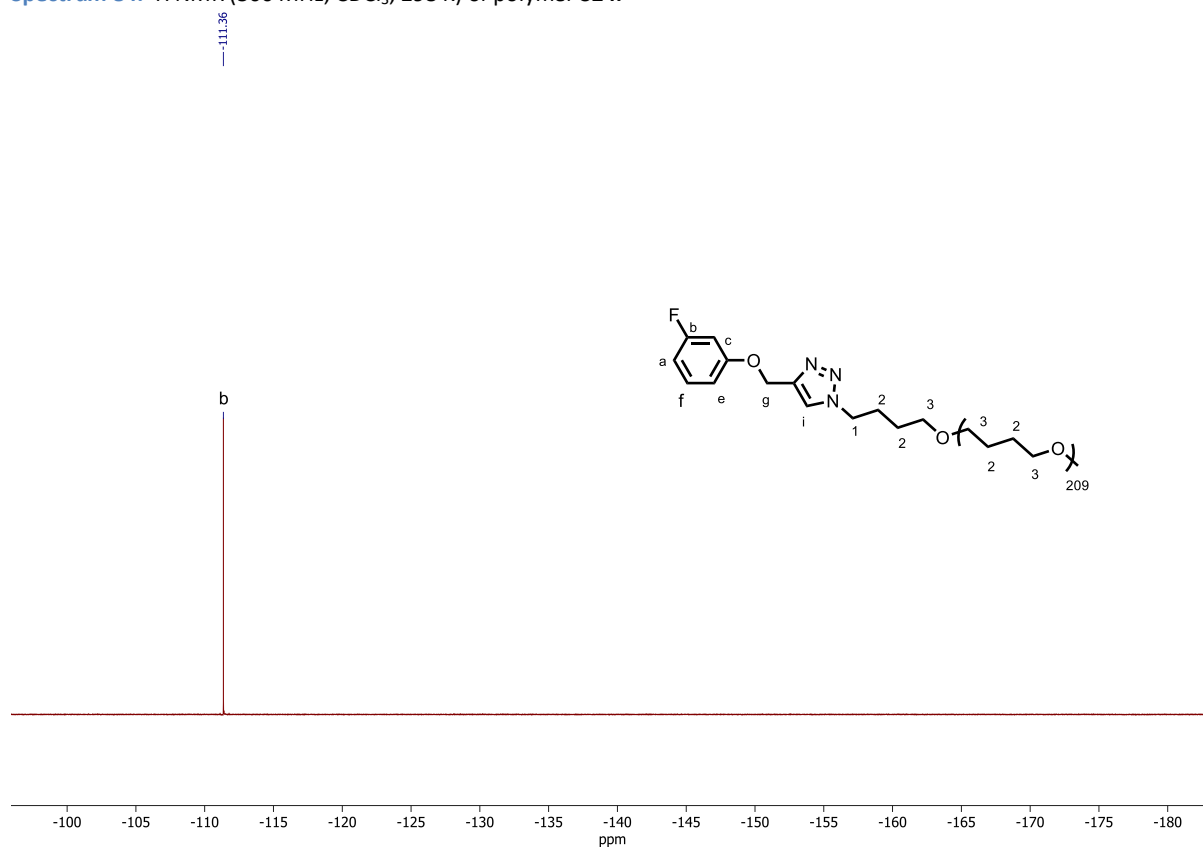
### 5.33 Spectra of S23



### 5.34 Spectra of S24



**Spectrum 84.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of polymer **S24**.

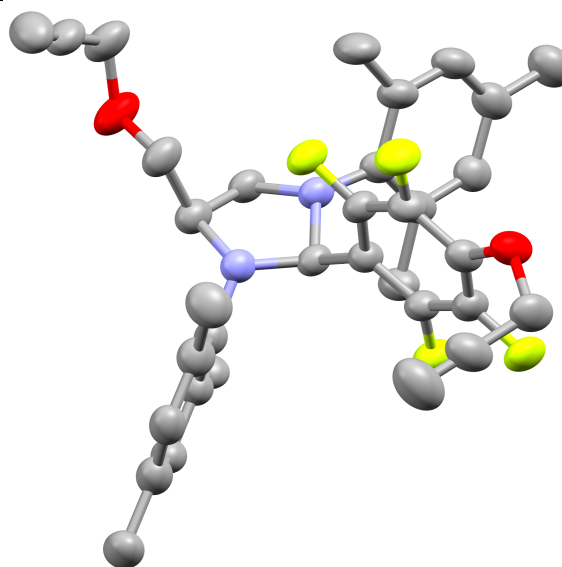


**Spectrum 85.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of polymer **S24**.

## 6 Crystal structure of **2<sub>H</sub>**

**Table 1.** Summary of crystal data for compound **2**.

|                                     |                                                                              |
|-------------------------------------|------------------------------------------------------------------------------|
| CCDC deposition number              | 1991781                                                                      |
| Identification code                 | <b>2<sub>H</sub></b>                                                         |
| Empirical formula                   | C <sub>34</sub> H <sub>34</sub> F <sub>4</sub> N <sub>2</sub> O <sub>2</sub> |
| Formula weight                      | 578.63                                                                       |
| Temperature/K                       | 150                                                                          |
| Crystal system                      | triclinic                                                                    |
| Space group                         | P -1                                                                         |
| a/Å                                 | 10.1213(6)                                                                   |
| b/Å                                 | 11.4077(7)                                                                   |
| c/Å                                 | 13.4595(10)                                                                  |
| α/°                                 | 75.271(6)                                                                    |
| β/°                                 | 84.031(6)                                                                    |
| γ/°                                 | 87.258(5)                                                                    |
| Volume/Å <sup>3</sup>               | 1494.46(17)                                                                  |
| Z                                   | 2                                                                            |
| ρ <sub>calc</sub> g/cm <sup>3</sup> | 1.286                                                                        |
| μ/mm <sup>-1</sup>                  | 0.806                                                                        |
| F(000)                              | 608.0                                                                        |
| Crystal size/mm <sup>3</sup>        | 0.25 x 0.20 x 0.04                                                           |
| Radiation                           | CuKα (λ = 1.54184)                                                           |
| 2θ range for data collection/°      | 4.008 to 72.590                                                              |
| Goodness-of-fit                     | 1.072                                                                        |
| R (reflections)                     | 0.0819 (4110)                                                                |
| wR2 (reflections)                   | 0.2699 (5579)                                                                |
| Flack parameter                     | Centrosymmetric                                                              |

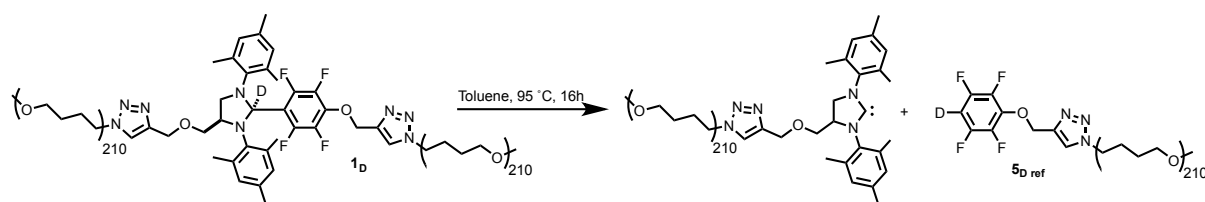


Crystal structure of **2<sub>H</sub>** showing 50% thermal ellipsoid probability.

## 7 Thermal Activation of Mechanophores

### 7.1 Thermal Activation of Polymer **1<sub>D</sub>**

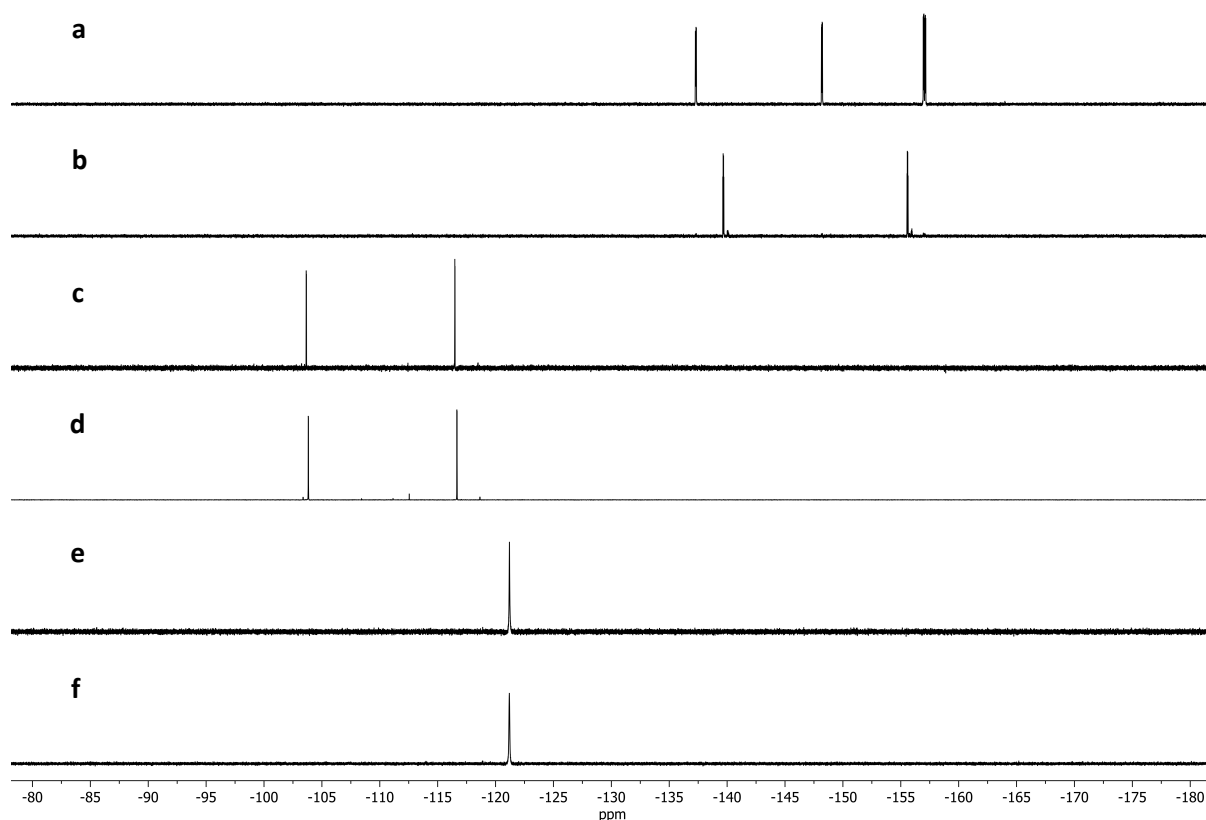
In order to get a  $^{19}\text{F}$  NMR spectrum for **5<sub>D ref</sub>**, we thermally activated polymer **1<sub>D</sub>**. Thermal activation of the compound results in only the concerted pathway being followed and hence forming only the deuterated analogue of **5**. The resulting  $^{19}\text{F}$  NMR spectrum can be seen in Figure S5. This procedure was carried out as follows: **1<sub>D</sub>** (50 mg) was dissolved in toluene (5 mL) and placed in a sealed microwave vial. The mixture was heated to 95 °C for 16 h; after cooling to room temperature, the mixture was condensed and allowed to dry thoroughly before being analysed.



### 7.2 Thermal Activation of **2<sub>H</sub>**, **S17**, and **S18**

We compared the thermal activation processes of the variably fluorinated small molecule mechanophores, **2<sub>H</sub>**, **S17**, and **S18**, in order to show that mechanical force allowed us access to previously unattainable reactions. The procedure for this was as follows: **2<sub>H</sub>**, **S17**, or **S18** (10 mg) was dissolved in xylenes (1 mL) in a sealed microwave vial. The mixture was heated to 130 °C for 24 h before being condensed and analysed by  $^{19}\text{F}$  NMR spectroscopy.

As expected, after heating **2<sub>H</sub>** showed essentially complete conversion to the corresponding tetrafluorobenzene derivative, **S4**. Both **S17** and **S18** showed no changes at all demonstrating their considerable thermal stability compared to **2<sub>H</sub>**. These results can be seen in Figure 3.

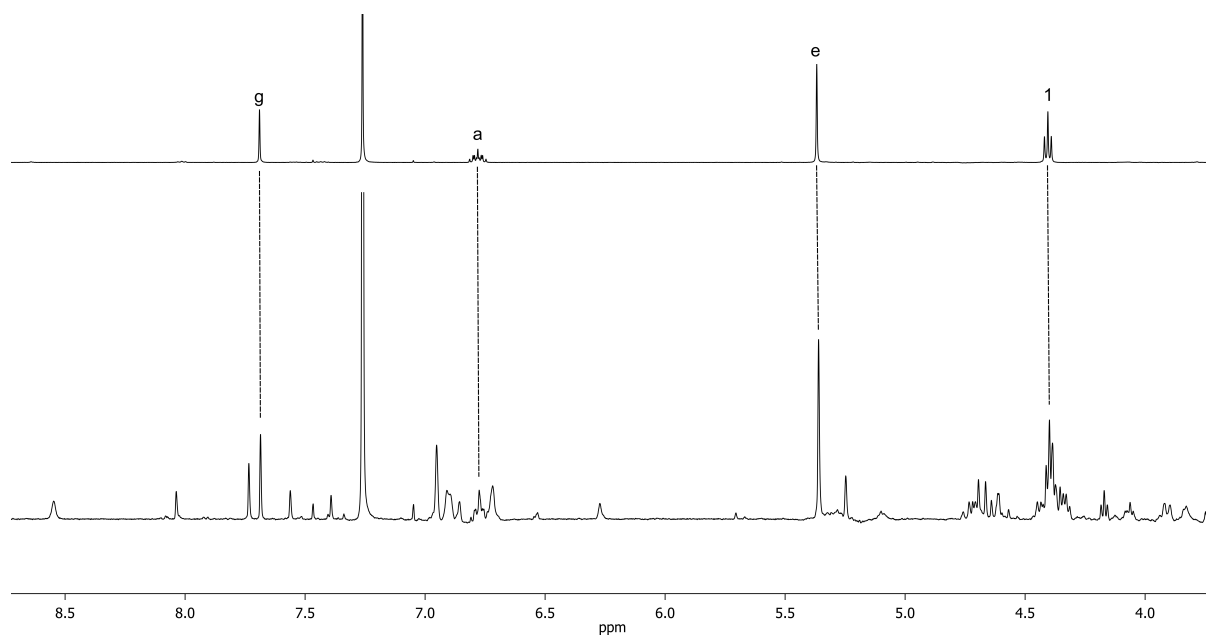


**Figure 3.**  $^{19}\text{F}$  NMR spectra (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) showing (a) **2<sub>H</sub>** before heating, (b) **2<sub>H</sub>** after heating at 130 °C for 24 h, (c) **S17** before heating, (d) **S17** after heating after heating at 130 °C for 24 h, (e) **S18** before heating, (f) **S18** after heating after heating at 130 °C for 24 h.

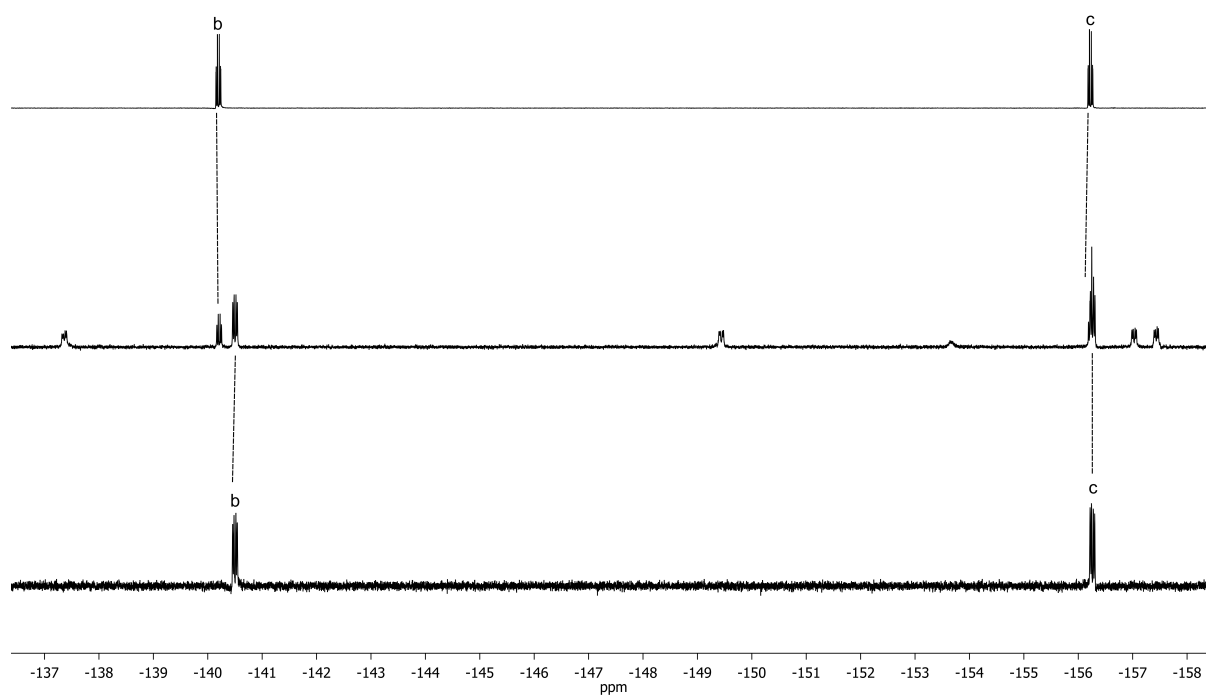
## 8 Sonication Experiments

All experiments were carried out using the same sonication conditions (20 KHz,  $15.6 \text{ W cm}^{-2}$ , 1 s ON / 1 s OFF, 5 – 10 °C).

Representative  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra for the cleavage of polymer **1<sub>H</sub>** can be seen in Figures S4 and S5 respectively. In all  $^{19}\text{F}$  NMR spectra, peaks belonging to the protonated tetrafluorobenzene species, **5<sub>H</sub>**, and the deuterated tetrafluorobenzene species, **5<sub>D</sub>**, were identified using the  $^{19}\text{F}$  NMR spectrum of **5<sub>H ref</sub>** along with that of **1<sub>D</sub>** after having been thermally activated (as described in Section 7).



**Figure 4.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ , 298 K) showing (top)  $5_{\text{H ref}}$  and (bottom) a representative sample of  $1_{\text{H}}$  post-sonication – taken from Section 8.6, Spectrum 88.

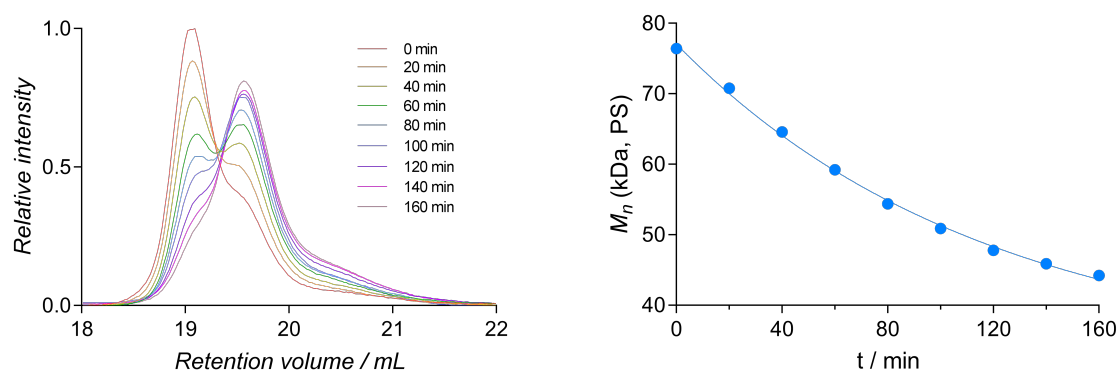


**Figure 5.**  $^{19}\text{F}$  NMR spectra (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) showing (top)  $5_{\text{H ref}}$ , (middle) a representative sample of  $1_{\text{H}}$  post-sonication – taken from Section 8.6, Spectrum 89 – and (bottom)  $5_{\text{D ref}}$  formed from  $1_{\text{D}}$  after thermal activation (see Section 7). The peaks between -140 and -141 ppm most clearly show the difference between  $5_{\text{H}}$  and  $5_{\text{D}}$ .



## 8.1 Sonication procedure for obtaining kinetic data

**1<sub>H</sub>** (15 mg) was dissolved in dry THF (15 mL) and added to a modified Suslick cell. Nitrogen was gently bubbled through the solution as it was sonicated. The solution was sonicated for 160 min with an aliquot (0.4 mL) taken before sonication and every 20 min of sonication time after for GPC analysis.



**Figure 6.** (Left) Normalised GPC traces taken over the course of a sonication experiment – the high mass peak (left) can be seen decreasing in intensity as the low mass peak (right) increases due to cleavage of the mechanophore. (Right) Graph showing the change in  $M_n$  of the polymer sample in the same experiment;  $t$  is given as the sonication time.

## 8.2 Standard sonication procedure

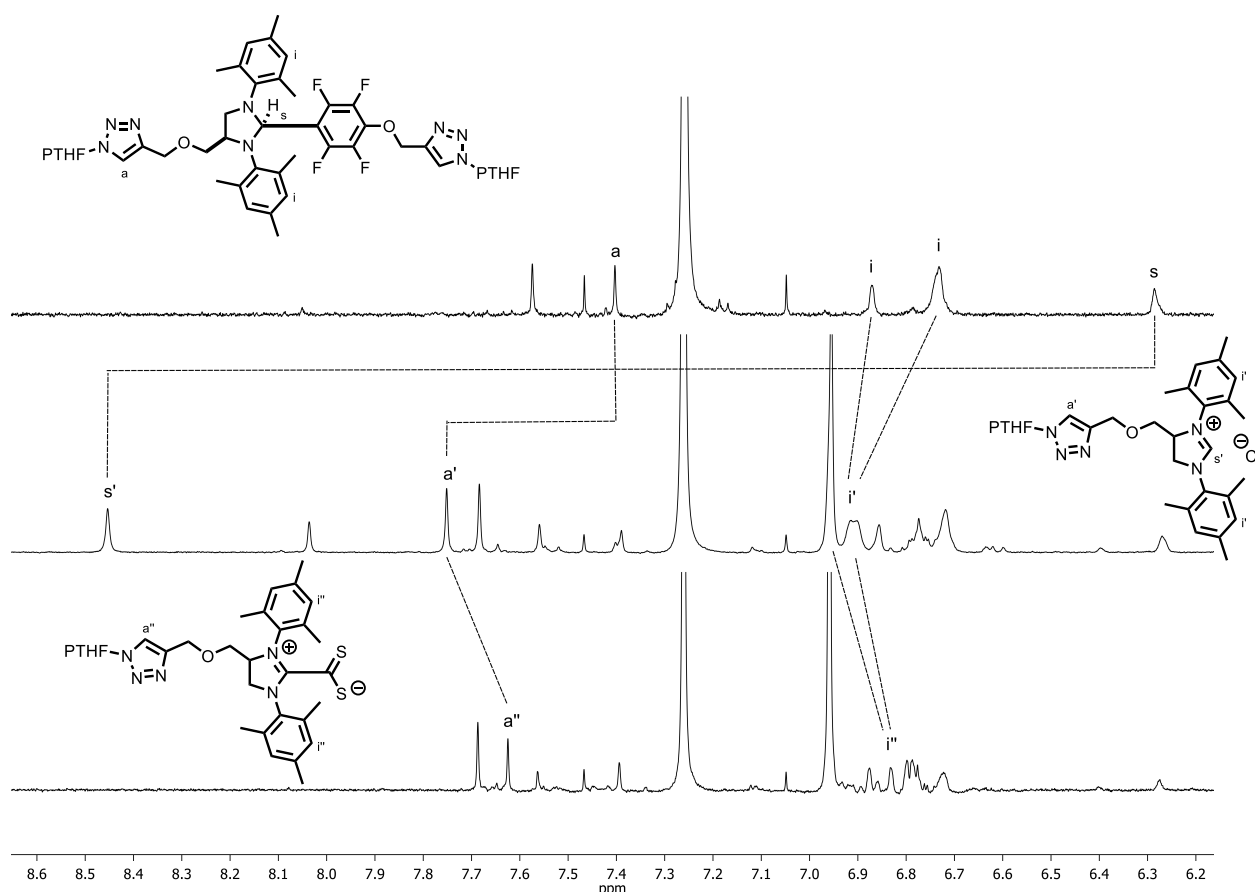
The specified polymer (70 mg) was dissolved in the specified solvent mixture (approx. 15 mL) and added to a modified Suslick cell. Nitrogen was gently bubbled through the solution as it was sonicated. After 180 min of sonication time, the mixture was undisturbed for 24 h to allow metal impurities to settle to the bottom of the cell. The solution was then carefully decanted to remove such impurities and condensed to give the crude polymer. After drying under high vacuum for an extended period of time (approximately 24 h), the polymer was washed with acetonitrile (5 mL) before drying again. The ratio of protonated and deuterated tetrafluorobenzene species (**5<sub>H</sub>** and **5<sub>D</sub>** respectively) was determined by  $^{19}\text{F}$  NMR.

**Table 2.** Sonication experiments carried out using **1<sub>H</sub>** and **1<sub>D</sub>** in various solvent systems along with the resulting ratio of protonated and deuterated tetrafluorobenzene species (**5<sub>H</sub>** and **5<sub>D</sub>** respectively) formed.

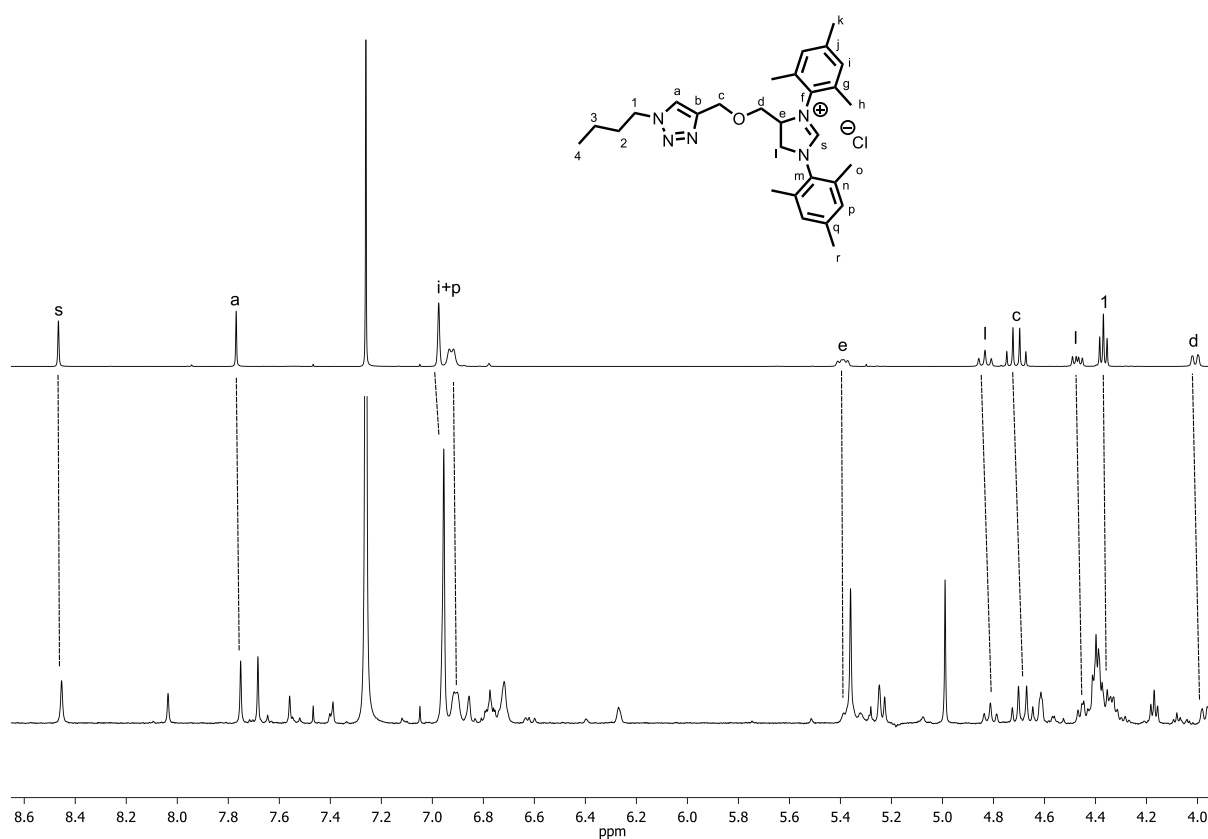
| Polymer              | Solvents                                                | <b>5<sub>H</sub></b> : <b>5<sub>D</sub></b> |
|----------------------|---------------------------------------------------------|---------------------------------------------|
| <b>1<sub>H</sub></b> | THF                                                     | 100:0                                       |
| <b>1<sub>H</sub></b> | THF/D <sub>2</sub> O (15:0.2)                           | 32:68                                       |
| <b>1<sub>D</sub></b> | THF/H <sub>2</sub> O (15:0.2)                           | 76:24                                       |
| <b>1<sub>H</sub></b> | THF-d <sub>8</sub> /benzene/H <sub>2</sub> O (1:14:0.2) | 95:5                                        |
| <b>1<sub>H</sub></b> | THF/methanol-d <sub>4</sub> (15:0.2)                    | 28:72                                       |
| <b>1<sub>D</sub></b> | THF/D <sub>2</sub> O (15:0.2)                           | 6:94                                        |
| <b>1<sub>H</sub></b> | THF/H <sub>2</sub> O (15:0.2)                           | 100:0                                       |
| <b>1<sub>D</sub></b> | THF                                                     | 78:22                                       |

### 8.3 Investigating the Imidazolidine Side of the Mechanophore

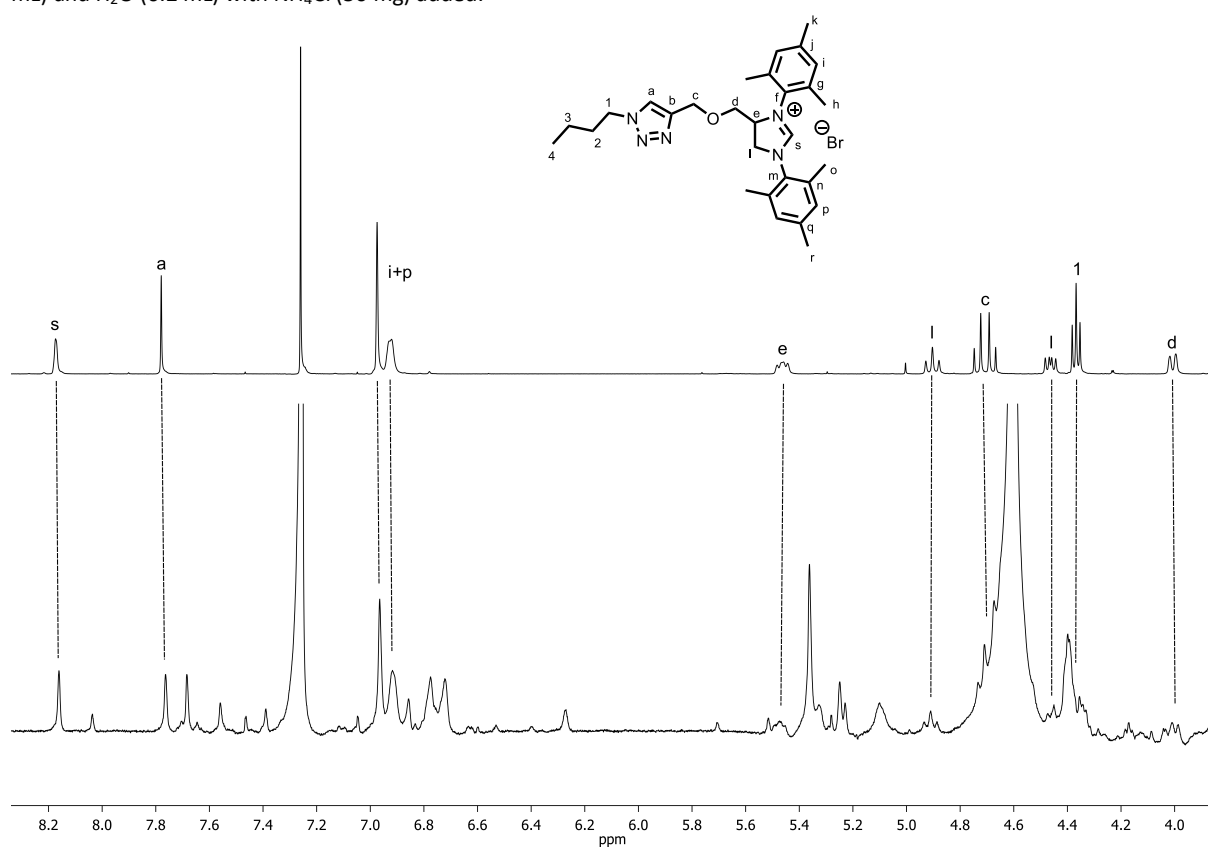
We decided to investigate the fate of the imidazolidinium salt that is formed when **1** cleaves through the majority heterolytic pathway. We noted one distinct peak in the post-sonication  $^1\text{H}$  NMR spectrum of **1<sub>H</sub>**, found at 8.55 ppm, that seemed particularly indicative of such a species and is likely shifted from the corresponding peak ( $\text{H}_s$ , 6.29 ppm) of **1<sub>H</sub>** pre-sonication. Additionally, a peak found at 7.73 ppm indicated a newly formed 1,4-triazole species with a large shift from the corresponding peak ( $\text{H}_a$ , 7.40 ppm) of pre-sonication **1<sub>H</sub>**. As we were unsure about what the counterion would be during a standard sonication experiment, we proposed that addition of a salt to the mixture during sonication would allow us to select the counterion. Sonication experiments were carried out as described in Section 8.2 in a mixture of THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL) with addition of either  $\text{NH}_4\text{Cl}$  (50 mg) or  $\text{LiBr}$  (50 mg); a notable upfield shift (approx. 0.4 ppm) of the aforementioned peak at 8.55 ppm is observed when  $\text{LiBr}$  is added while addition of  $\text{NH}_4\text{Cl}$  results in only a minor shift (approx. 0.1 ppm, Figure 7). Aside from these shifts the post-sonication spectra look very similar, a good indicator that the only difference is indeed the counterion. Of course, comparison of these spectra with synthesised reference imidazolidinium chloride (Figure 8) and bromide (Figure 9) salts confirmed the presence of these species post-sonication.



**Figure 7.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ , 298 K) showing (top) **1<sub>H</sub>**, (middle) **1<sub>H</sub>** after 180 min of sonication in THF with  $\text{H}_2\text{O}$  (0.2 mL) and  $\text{NH}_4\text{Cl}$  (50 mg) added and (bottom) **1<sub>H</sub>** after 180 min of sonication in THF with  $\text{NH}_4\text{Cl}$  (50 mg) added followed by a separate reaction with  $\text{NaH}$  and  $\text{CS}_2$  in dry THF.



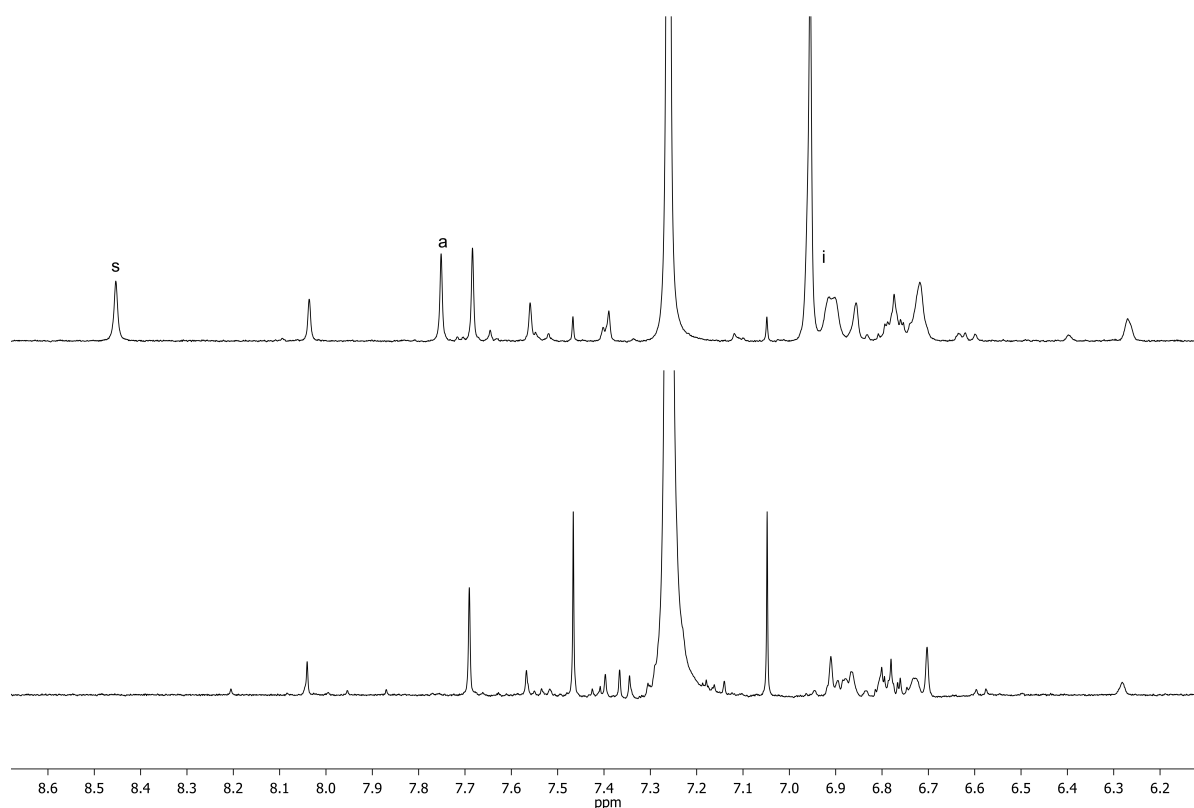
**Figure 8.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ , 298 K) showing (top) **6<sub>ref</sub>** and (bottom) **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL) with  $\text{NH}_4\text{Cl}$  (50 mg) added.



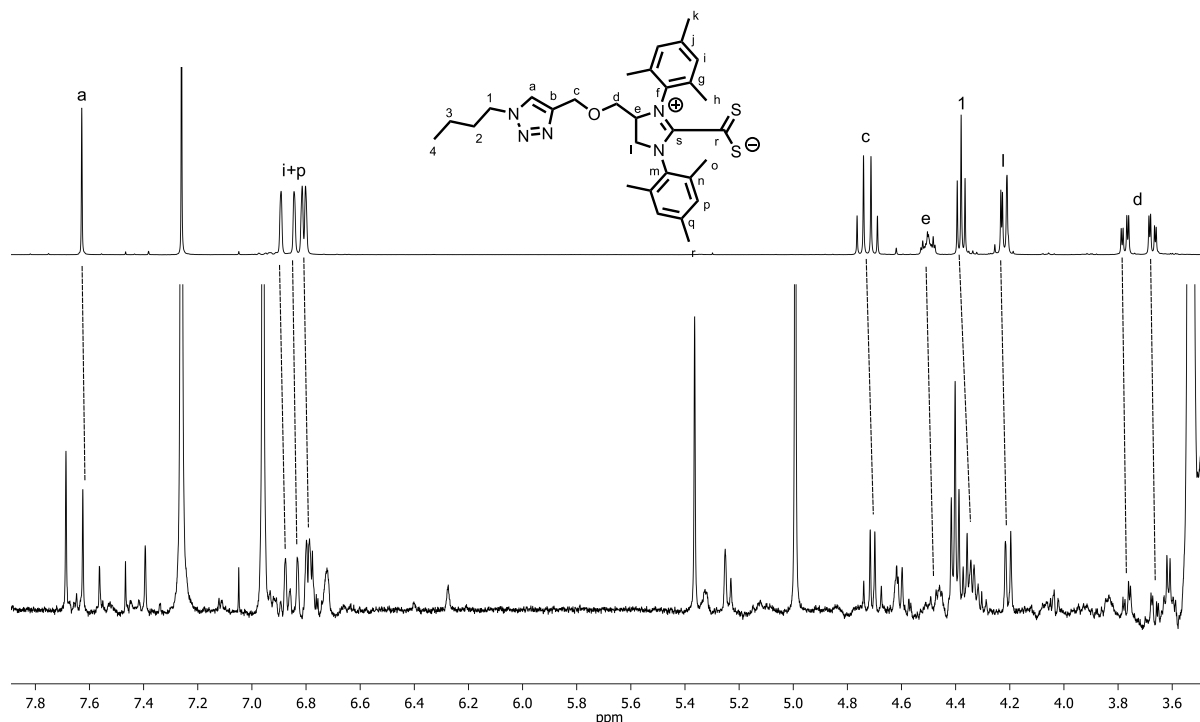
**Figure 9.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ , 298 K) showing (top) **S12** and (bottom) **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL) with  $\text{LiBr}$  (50 mg) added.

In order to further confirm the presence of the imidazolidinium species we proposed the idea that we could deprotonate the post-sonication in order to form the free carbene, much as could be done for any commercially available or synthesised such salt. We dissolved the crude post-sonication polymer in dry THF (5 mL) and added NaH (60% in mineral oil, 5 mg); the mixture was stirred for 1 h before being condensed. After drying the polymer was washed with acetonitrile (5 mL) and left to dry further under vacuum. As desired analysis of this crude mixture showed complete disappearance of the identified peaks (Figure 10) indicating our previous observations as being correct.

We also decided to check that the free carbene was actually the product of such a deprotonation reaction. We proposed a trapping reaction using CS<sub>2</sub> as the free carbene would be expected to react rapidly with this compound forming a stable zwitterionic product. The reaction was carried out as described above but with CS<sub>2</sub> (0.2 mL) present before addition of NaH. As expected, deprotonation of the crude post-sonication polymer in the presence of CS<sub>2</sub> followed by analysis of the resulting polymer material showed the presence of the desired species when compared with a synthesised reference compound (Figure 11). It was noted that during the reaction, addition of NaH immediately turned the solution slightly yellow, a further indicator of such a product being formed.

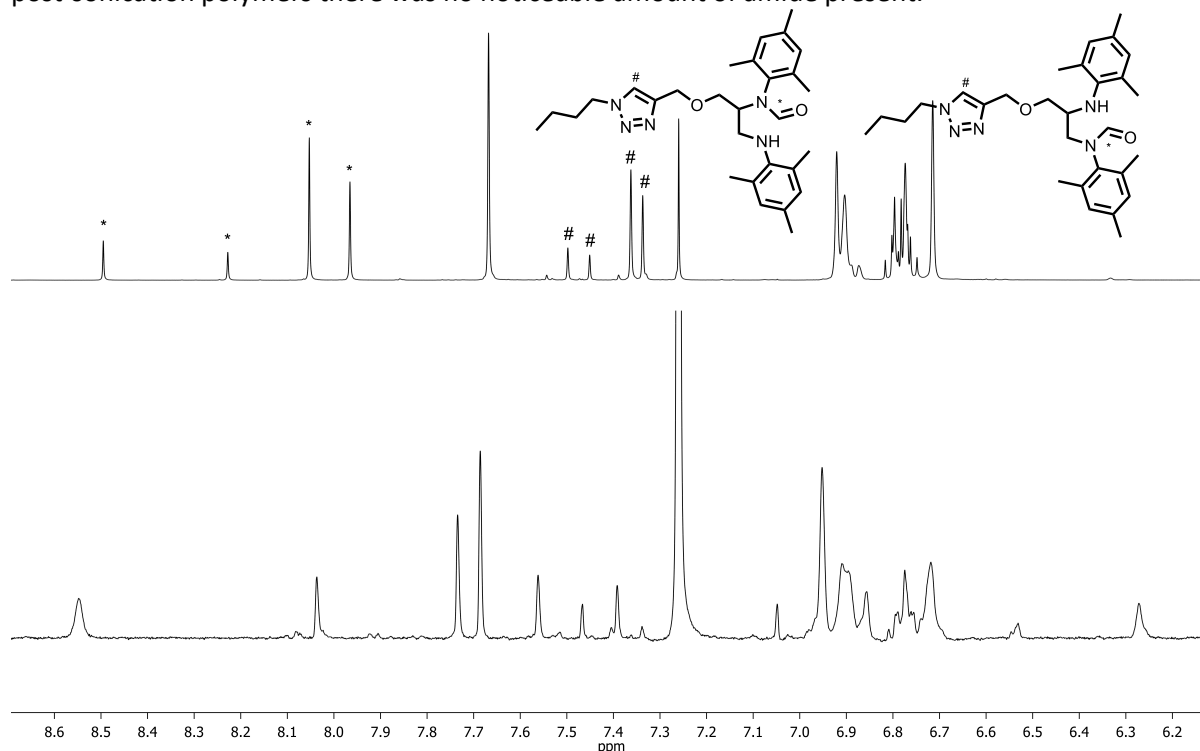


**Figure 10.** <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>, 298 K) showing (top) **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL) with NH<sub>4</sub>Cl (50 mg) added and (bottom) the same sample after reaction with NaH (60% in mineral oil, 5 mg) in THF (5 mL).



**Figure 11.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ , 298 K) showing (top) **7<sub>ref</sub>** and (bottom) **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL) with  $\text{NH}_4\text{Cl}$  (50 mg) added followed by a separate reaction with NaH (60% in mineral oil, 5 mg) and  $\text{CS}_2$  (0.2 mL) in dry THF (5 mL).

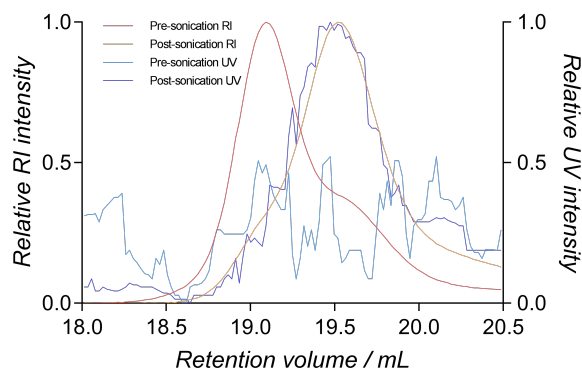
Finally, we checked to see if there was any hydrolysis, of either the imidazolidinium salt or free carbene, occurring during sonication. A synthesised reference compound, **S14**, utilising *n*-butyl chains in place of PTHF was thermally activated (as described in Section 7) in the presence of water; after condensing and drying the reaction mixture, the crude material was analysed allowing us to observe the respective amide compounds (Figure 12). Using this information, we found that in the post-sonication polymers there was no noticeable amount of amide present.



**Figure 12.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ , 298 K) showing (top) **S14** after thermal activation in toluene (1 mL) and  $\text{H}_2\text{O}$  (0.1 mL) and (bottom) **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL).

## 8.4 Sonication with DPPH

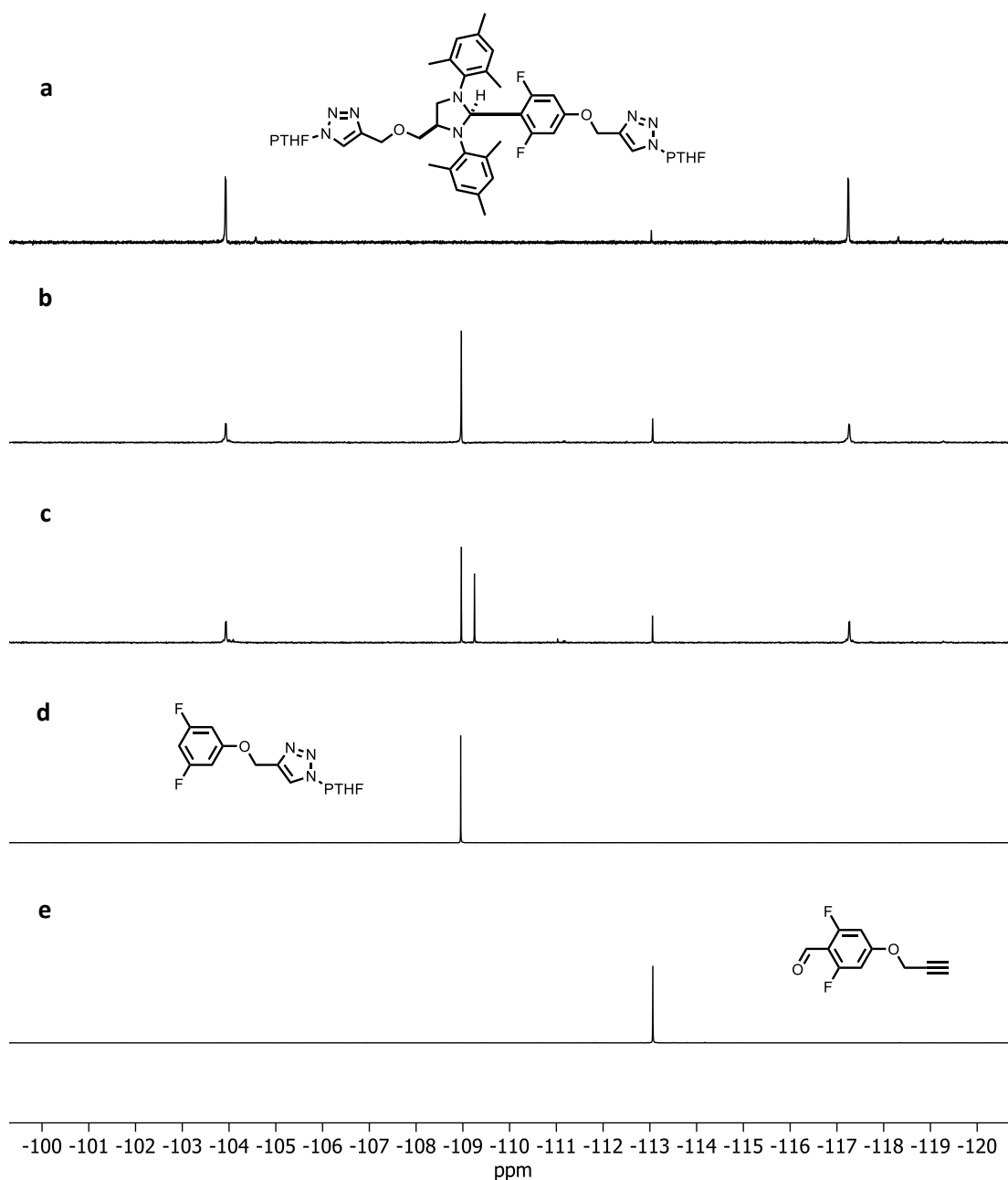
To further support the occurrence of a homolytic pathway during mechanical cleavage of **1<sub>H</sub>**, we employed 2,2-diphenyl-1-picrylhydrazyl (DPPH) as a radical trapping agent. As shown through <sup>19</sup>F NMR analysis of post-sonication mixtures, the homolytic pathway appears to be occurring for only 5% of cleavage events, a level that would make the observation of a DPPH-trapped species very challenging by <sup>1</sup>H NMR. Instead, we can analyse the cleavage of the polymer by GPC and compare the refractive index detection with that from the UV channel (Figure 13). DPPH being highly UV active means any trapped molecules at the end of a cleaved polymer will be observed when these chains are eluted during GPC analysis. Indeed, we observed such a peak in the UV GPC trace (320 nm) corresponding to the cleaved polymer.



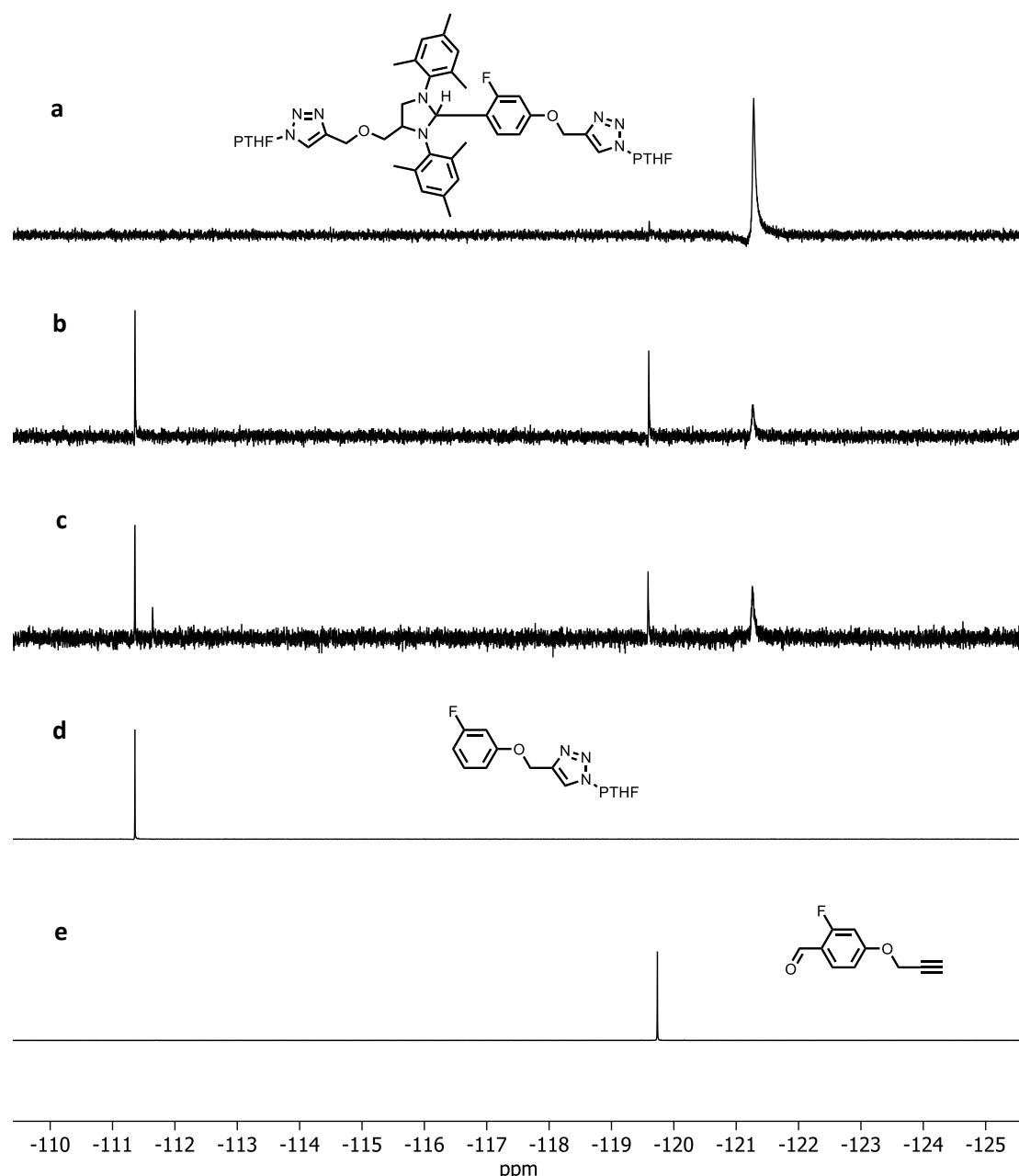
**Figure 13.** GPC traces comparing (red) **1<sub>H</sub>** pre-sonication in the RI channel, (orange) **1<sub>H</sub>** post-sonication, in THF (15 mL) with DPPH (50 mg) added, in the RI channel, and (yellow) **1<sub>H</sub>** post-sonication, in THF with DPPH (50 mg) added, in the UV channel (320 nm).

## 8.5 Sonication Experiments using Mono- and Difluoro Mechanophore Derivatives

The extent to which the cleavage of a difluorinated analogue of the mechanophore, **8a**, and a monofluorinated analogue, **8b**, went through the three different established pathways were investigated using a similar set of sonication experiments to those for polymer **1**. The sonication experiments were carried out in the manner described in Section 8.2. Compounds **S23** and **S24** were used as references for the protonated mono- and difluorobenzene compounds respectively that were expected to form post-cleavage. Due to the inability to synthesise deuterated analogues of these reference structures (**S23<sub>D</sub>** and **S24<sub>D</sub>**) being presumably highly arduous the peaks corresponding to these species are assumed from their chemical shifts relative to the protonated analogues; further evidence of the identity of these peaks can be found in their absence when no deuterium source is present in the sonication mixture. It is worth noting that both **8a** and **8b** do exhibit some decomposition when in solution leading to gradual formation of their precursor benzaldehydes.



**Figure 14.**  $^{19}\text{F}$  NMR spectra (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) showing (a) **8a**, (b) a representative sample of **8a** post-sonication – taken from Section 8.6, Spectrum 104 – in which the sonication had no source of deuterium, (c) a representative sample of **8a** post-sonication – taken from Section 8.6, Spectrum 106 – in which the sonication had a source of deuterium in the form of  $\text{D}_2\text{O}$ , (d) reference difluorobenzene compound **S23**, (e) precursor benzaldehyde **S15**.



**Figure 15.**  $^{19}\text{F}$  NMR spectra (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) showing (a) **8b**, (b) a representative sample of **8b** post-sonication – taken from Section 8.6, Spectrum 110 – in which the sonication had no source of deuterium, (c) a representative sample of **8b** post-sonication – taken from Section 8.6, Spectrum 112 – in which the sonication had a source of deuterium in the form of  $\text{D}_2\text{O}$ , (d) reference fluorobenzene compound **S24**, (e) precursor benzaldehyde **S16**.

As with the sonication experiments for **1<sub>H</sub>** and **1<sub>D</sub>**, the extent of protonation and deuteration of the resulting benzene structure post-sonication was determined by integration of the relevant peaks in the  $^{19}\text{F}$  NMR spectra. Experiments were carried out to determine the extent of the heterolytic pathway – 45% for **8a**, shown in Table 3, Entry 2 and 25% for **8b**, shown in Table 4, Entry 2 – and homolytic pathway – <5% for **8a**, shown in Table S3, Entry 3 and <5% for **8b**, shown in Table 4, Entry 3 – for both **8a** and **8b**. It is worth mentioning that, although the integrations of the spectra for determining the homolytic pathway of each mechanophore suggest 0% cleavage, limitations of the sensitivity of the instruments used might mean we simply cannot observe the result in this instance. The extent of the concerted pathway can then be determined simply as the remaining portion of cleavage – 55% for **8a** and 75% for **8b**.



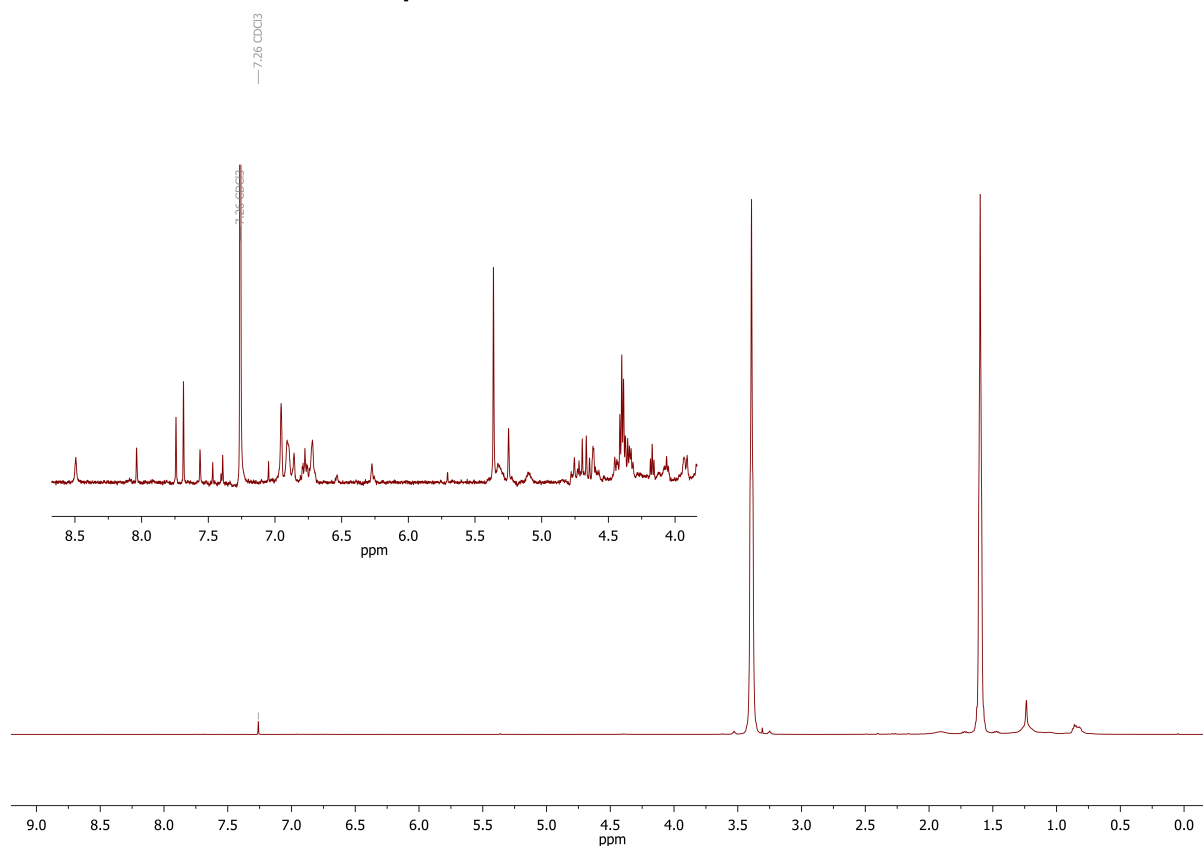
**Table 3.** Sonication experiments carried out using **8a** in various solvent systems along with the resulting ratio of protonated and deuterated difluorobenzene species (**S23<sub>H</sub>** and **S23<sub>D</sub>** respectively) formed.

| Entry | Solvents                                                | <b>S23<sub>H</sub></b> : <b>S23<sub>D</sub></b> |
|-------|---------------------------------------------------------|-------------------------------------------------|
| 1     | THF/H <sub>2</sub> O (15:0.2)                           | 100:0                                           |
| 2     | THF/D <sub>2</sub> O (15:0.2)                           | 55:45                                           |
| 3     | THF-d <sub>8</sub> /benzene/H <sub>2</sub> O (1:14:0.2) | 100:0                                           |

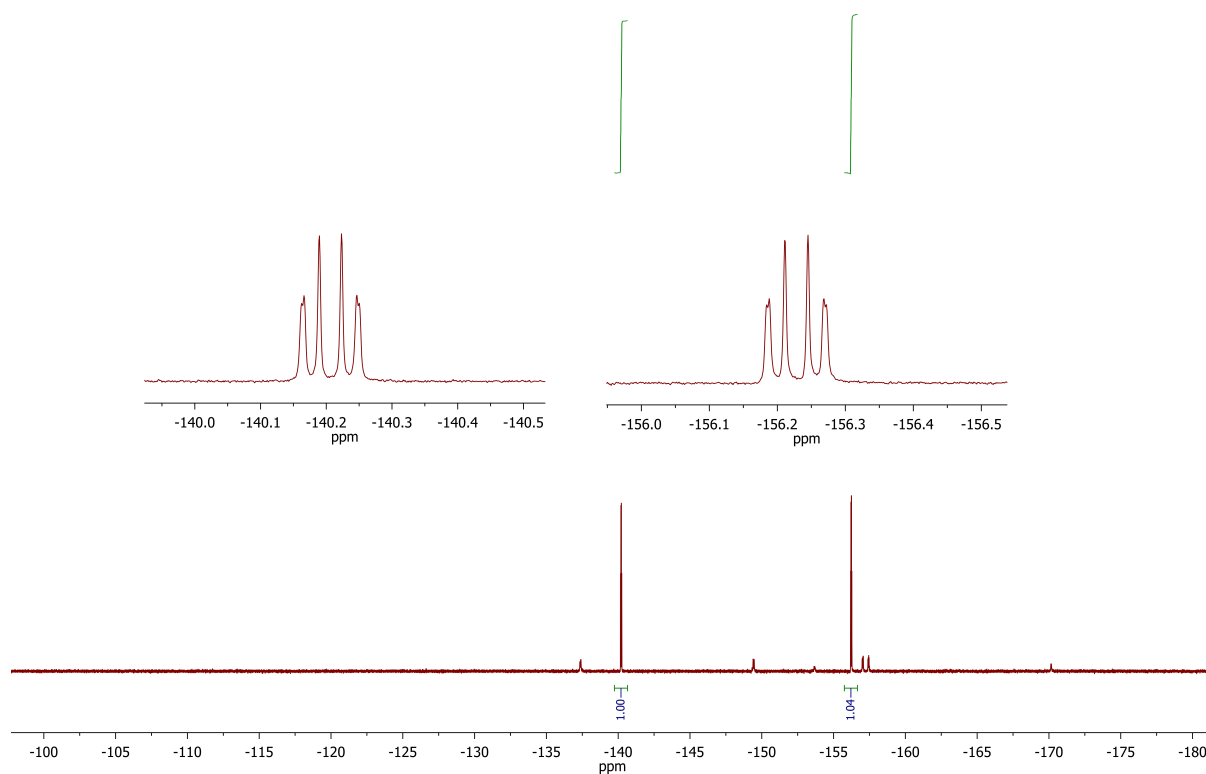
**Table 4.** Sonication experiments carried out using **8b** in various solvent systems along with the resulting ratio of protonated and deuterated fluorobenzene species (**S24<sub>H</sub>** and **S24<sub>D</sub>** respectively) formed.

| Entry | Solvents                                                | <b>S24<sub>H</sub></b> : <b>S24<sub>D</sub></b> |
|-------|---------------------------------------------------------|-------------------------------------------------|
| 1     | THF/H <sub>2</sub> O (15:0.2)                           | 100:0                                           |
| 2     | THF/D <sub>2</sub> O (15:0.2)                           | 75:25                                           |
| 3     | THF-d <sub>8</sub> /benzene/H <sub>2</sub> O (1:14:0.2) | 100:0                                           |

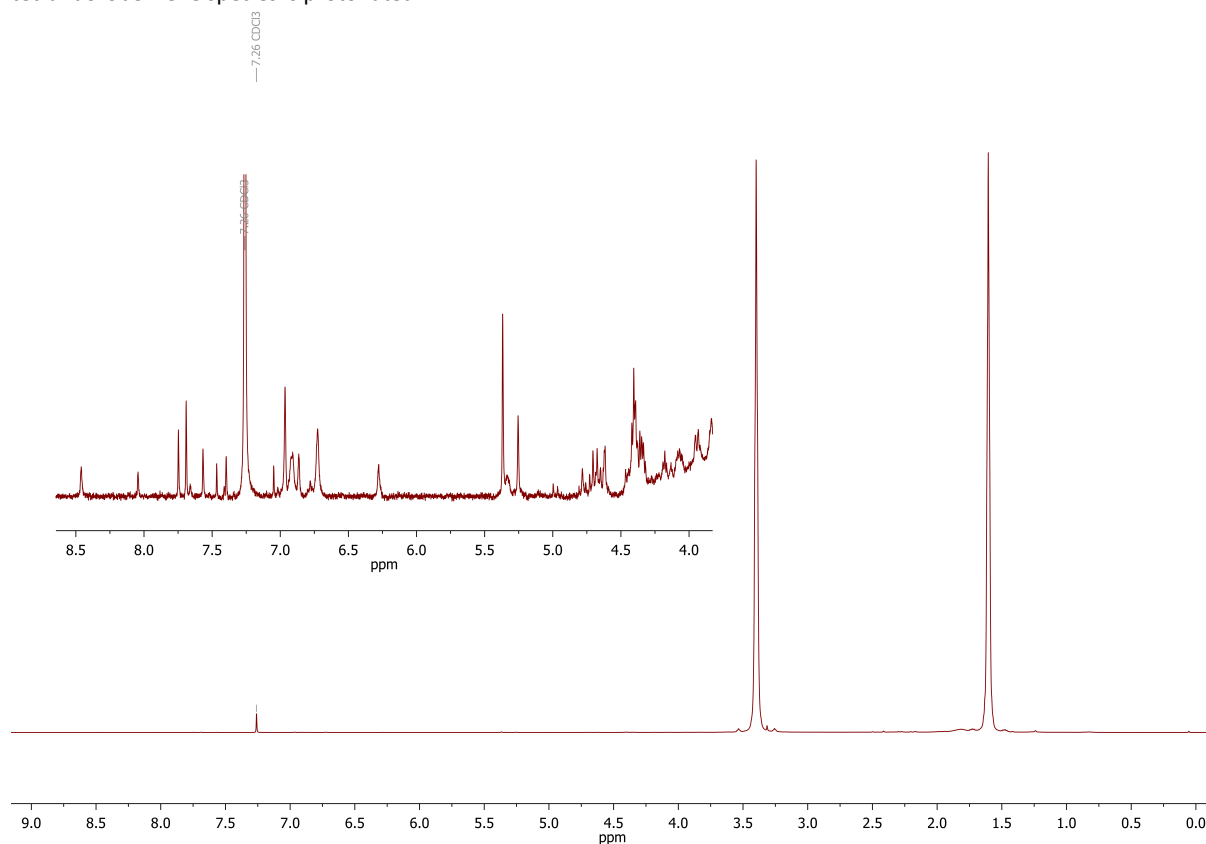
## 8.6 Post-Sonication NMR Spectra



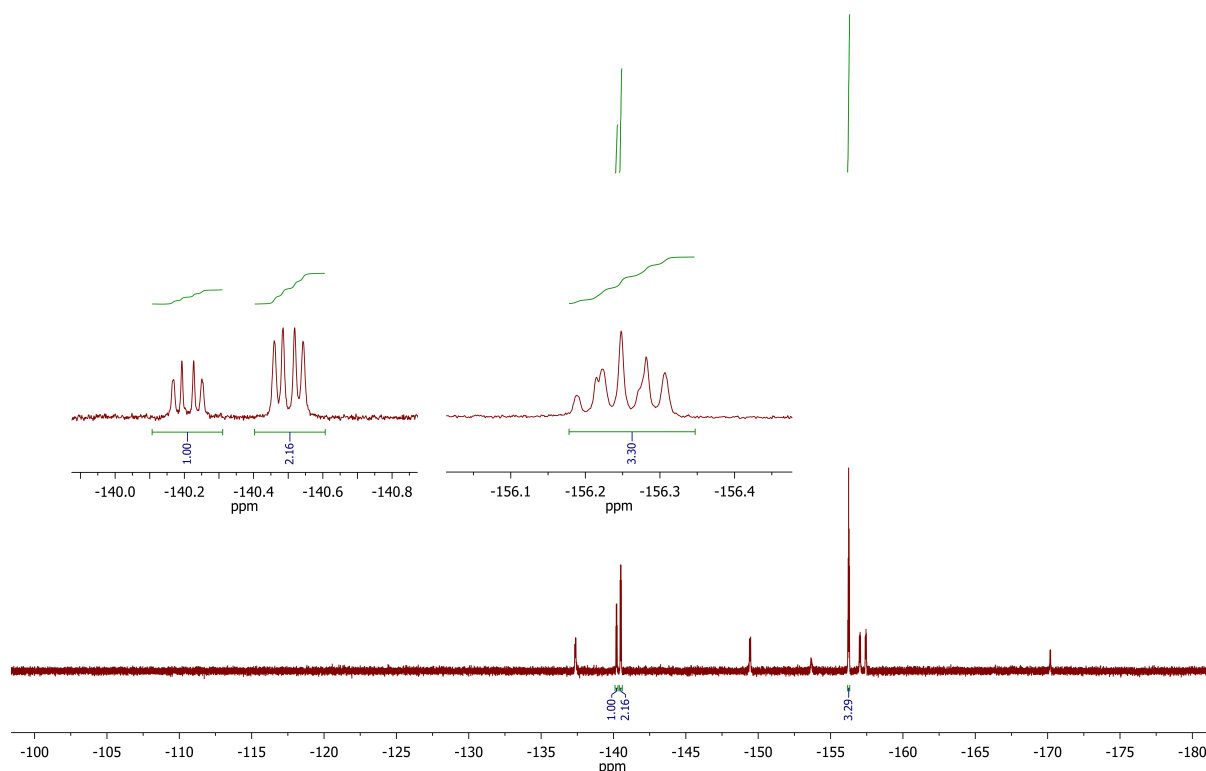
**Spectrum 86.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL).



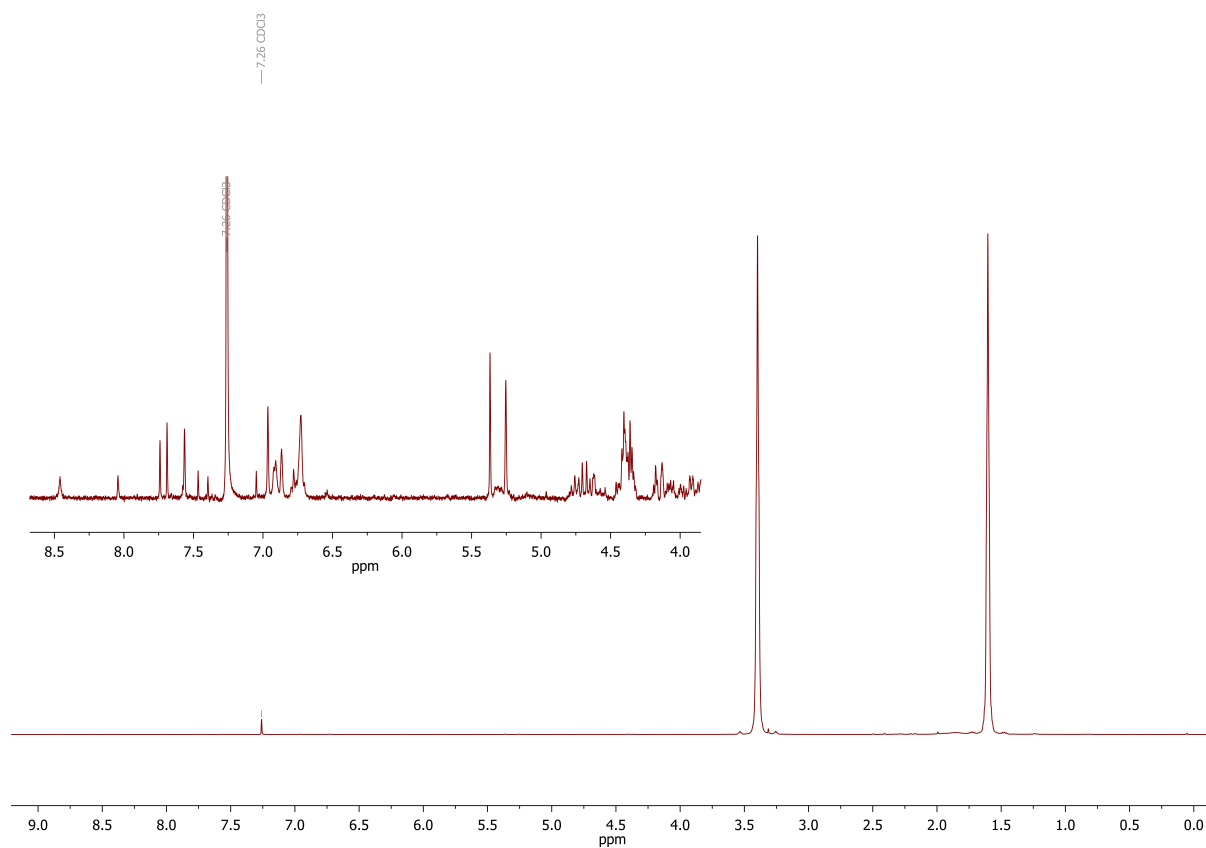
**Spectrum 87.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL). 100% of the formed tetrafluorobenzene species is protonated.



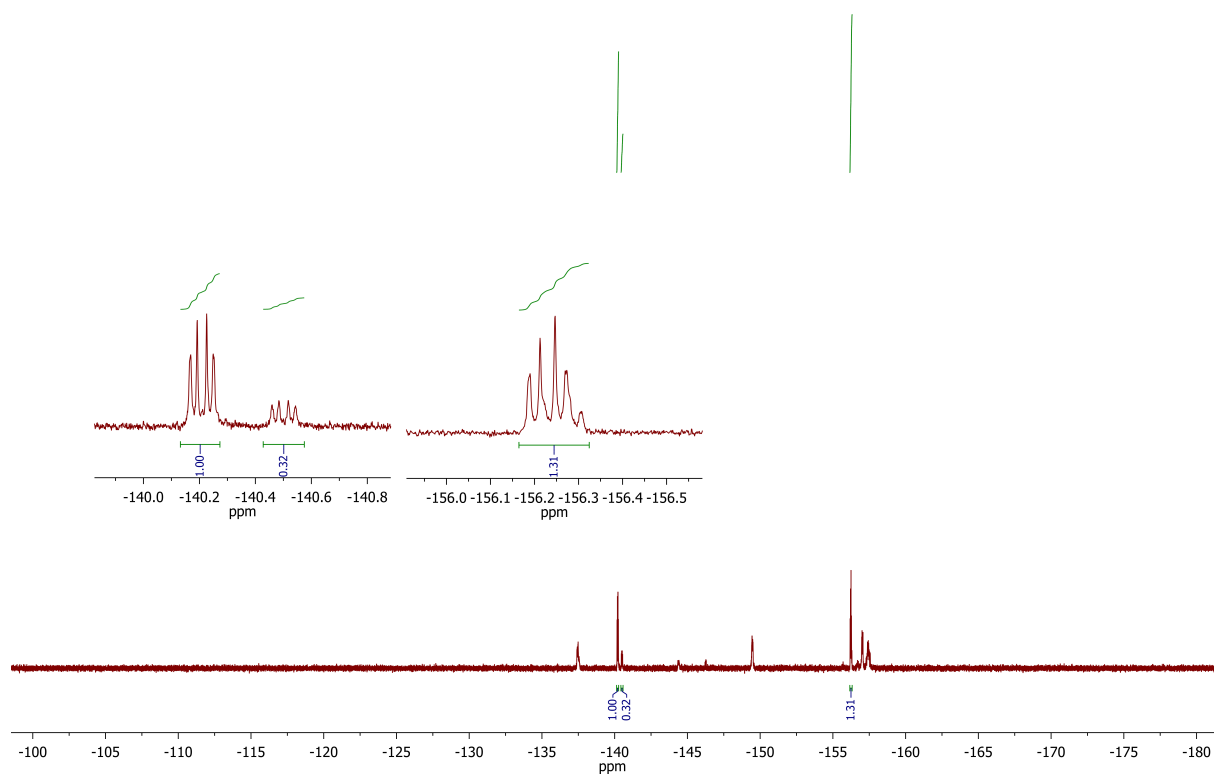
**Spectrum 88.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL).



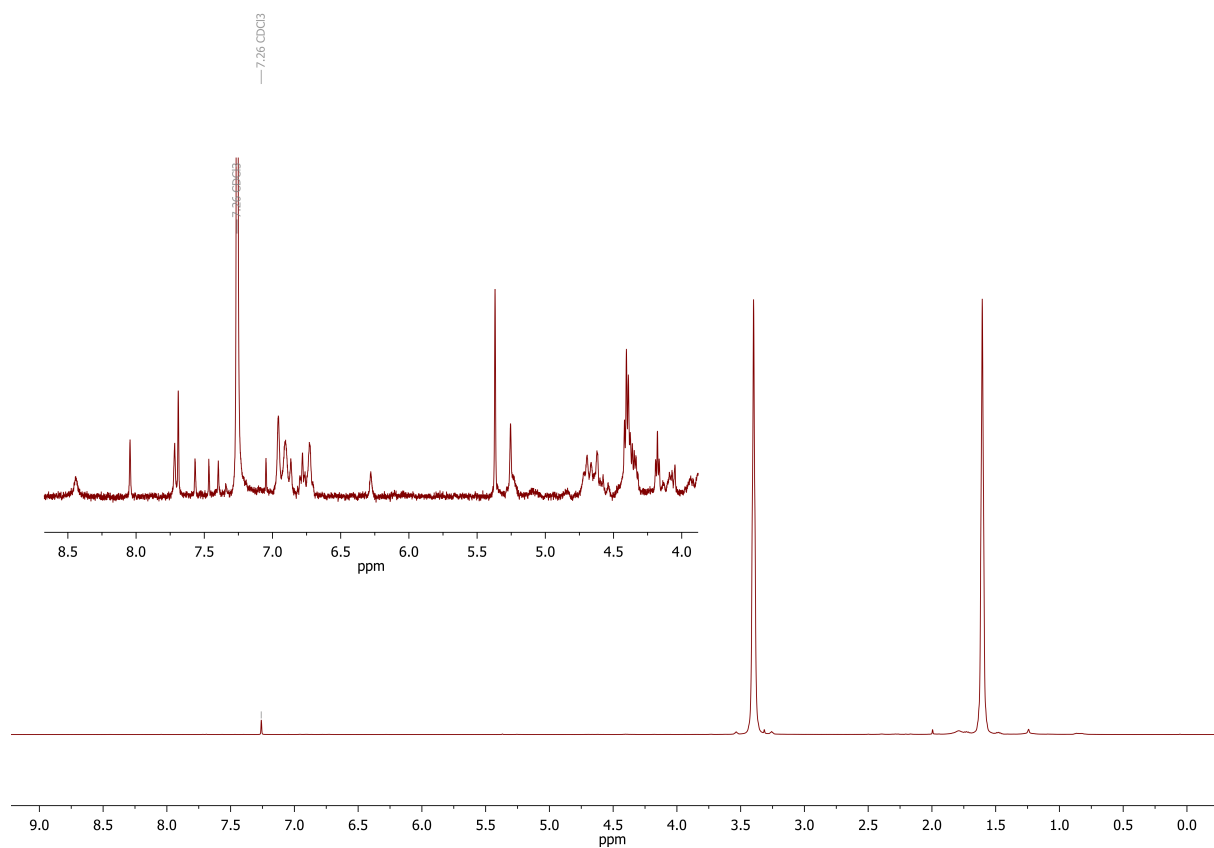
**Spectrum 89.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL). Approximately 68% of the tetrafluorobenzene species formed is deuterated.



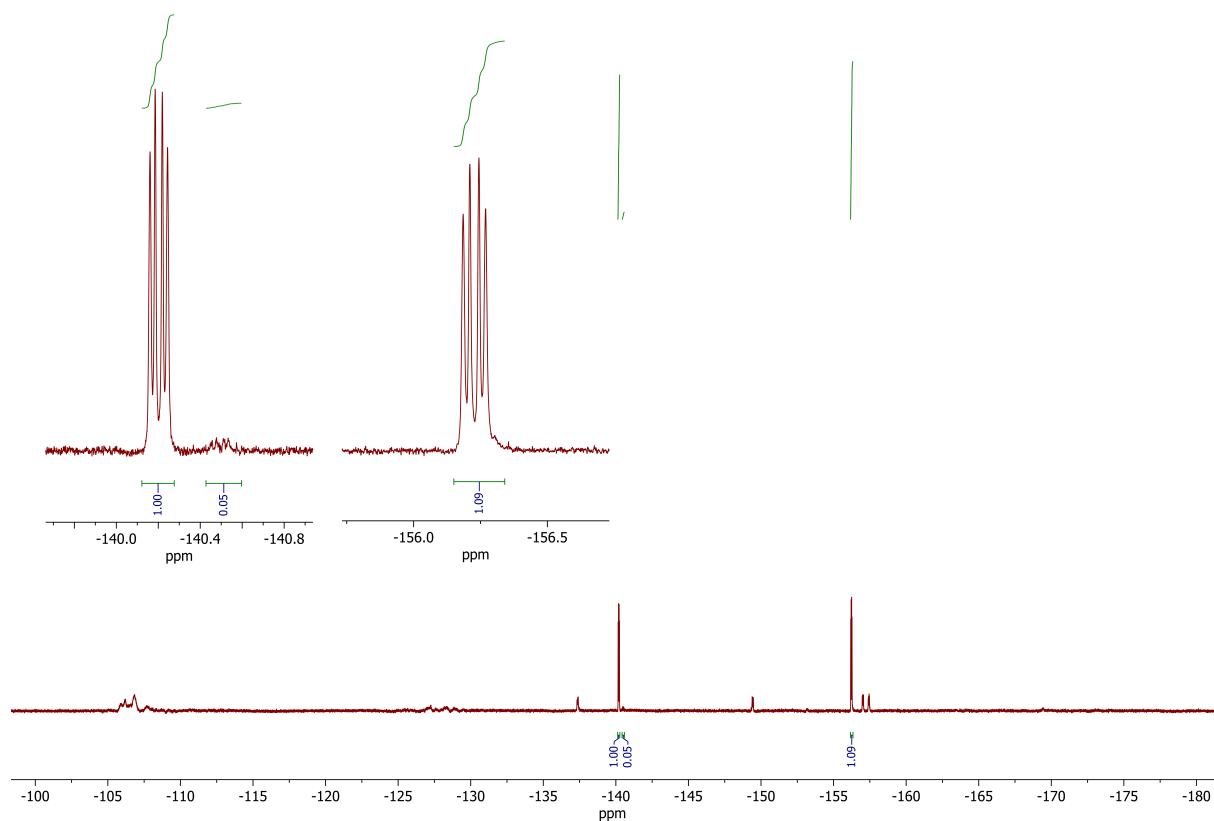
**Spectrum 90.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>D</sub>** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL).



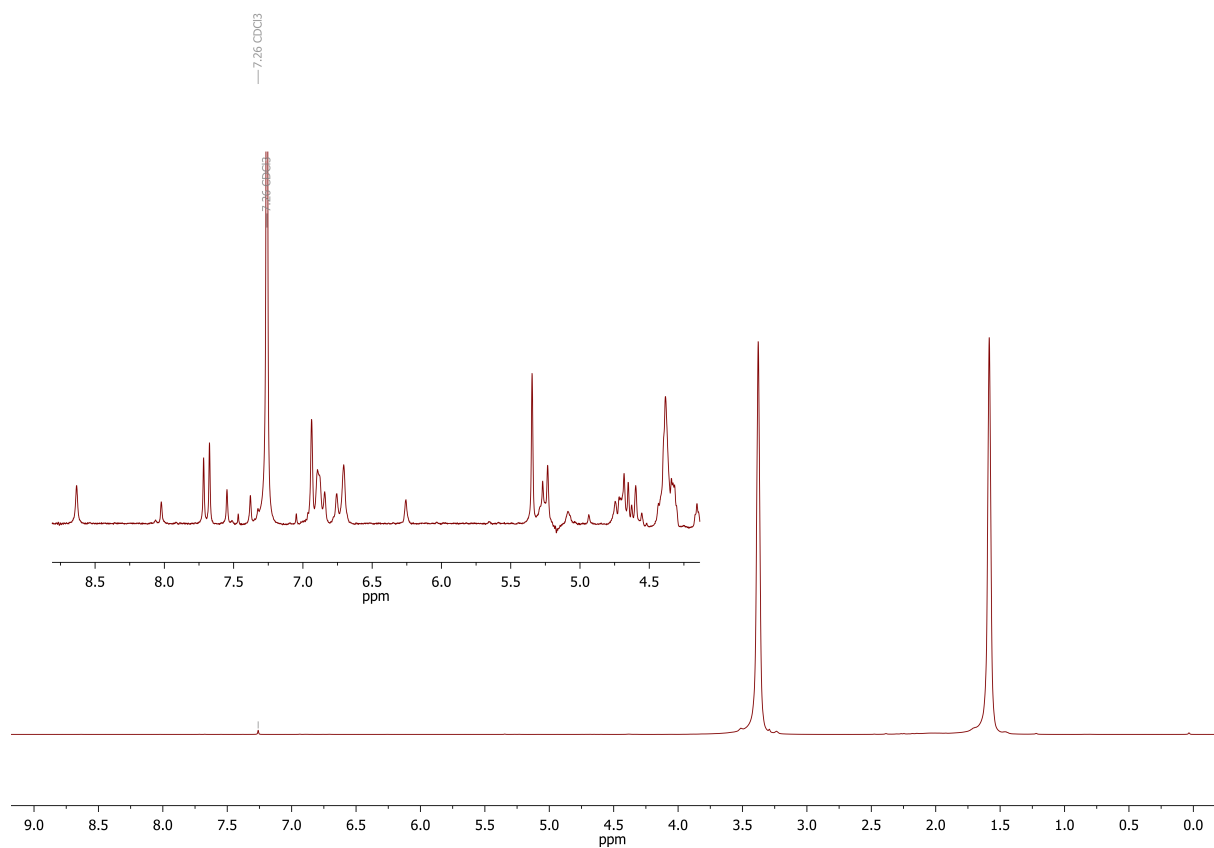
**Spectrum 91.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1D** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL). Approximately 24% of the tetrafluorobenzene species formed is deuterated.



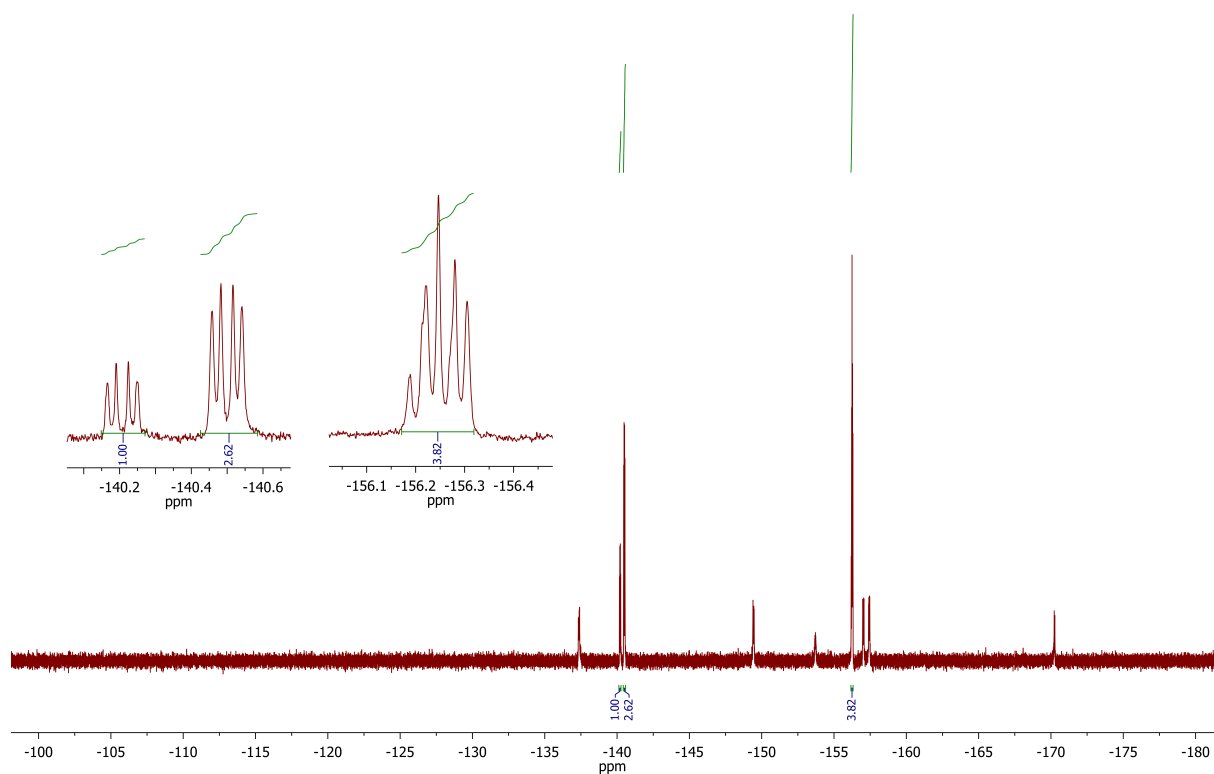
**Spectrum 92.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1H** after 180 min of sonication in  $\text{THF-d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL).



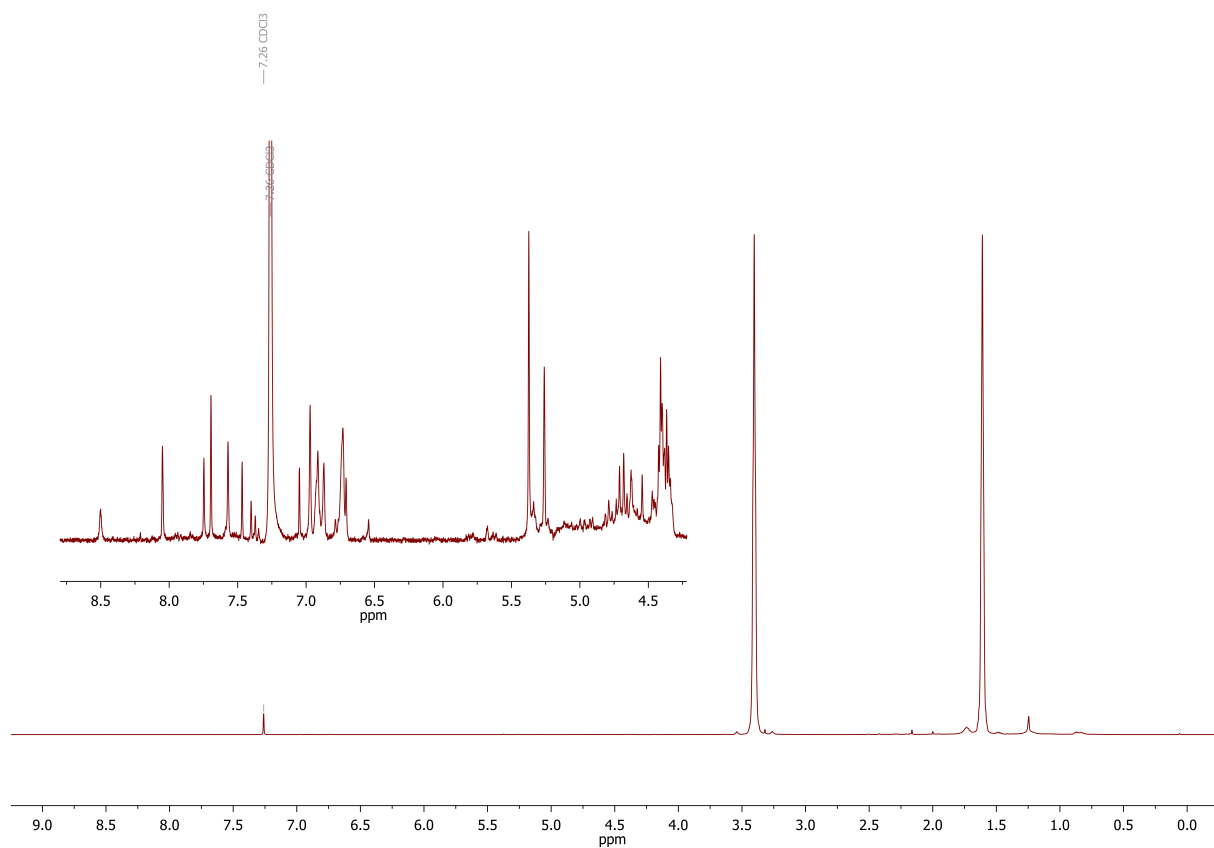
**Spectrum 93.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL). Approximately 5% of the tetrafluorobenzene species formed is deuterated.



**Spectrum 94.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and methanol- $\text{d}_4$  (0.2 mL).

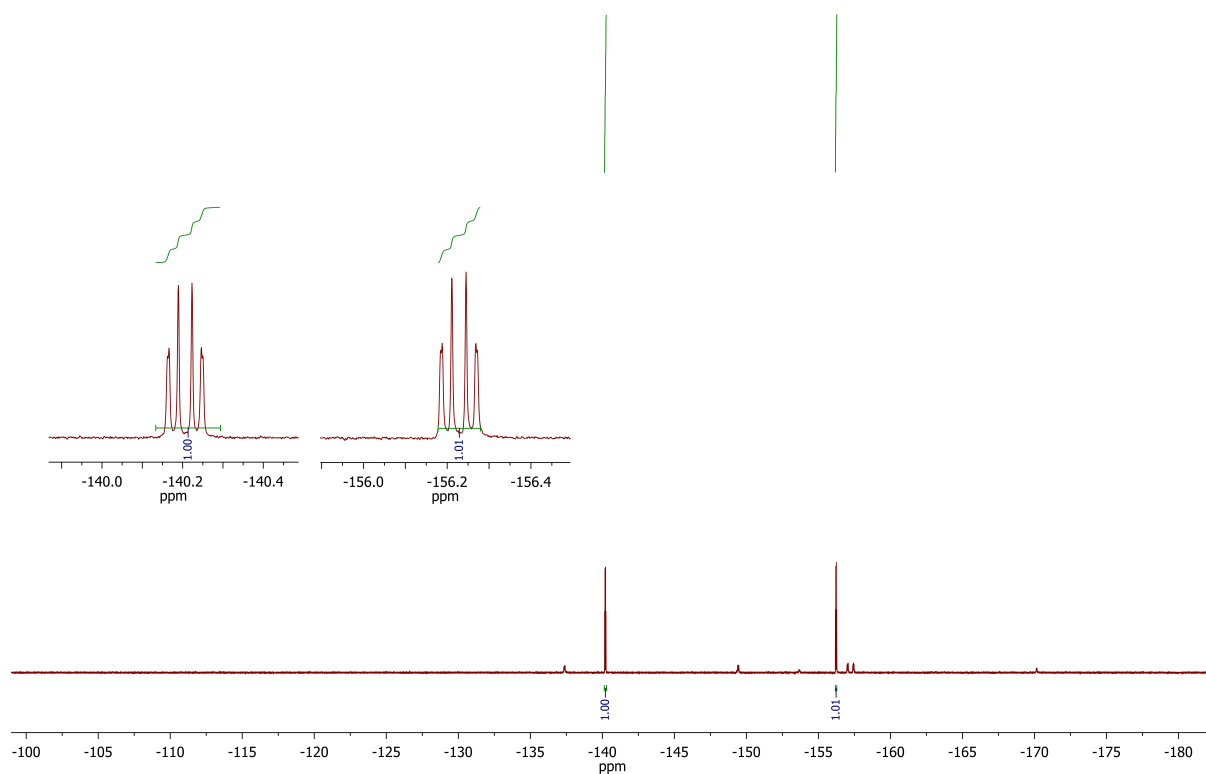


**Spectrum 95.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and methanol- $\text{d}_4$  (0.2 mL). Approximately 72% of the tetrafluorobenzene species formed is deuterated.

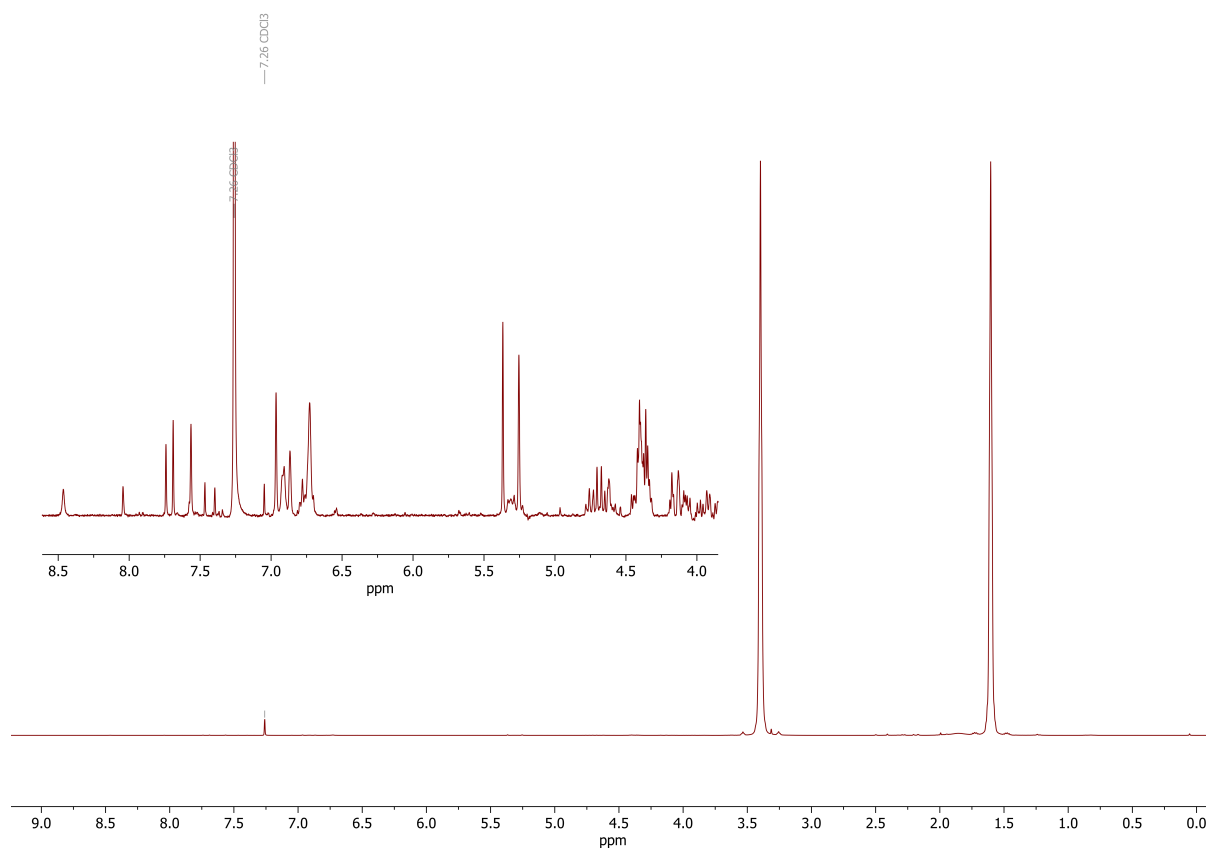


**Spectrum 96.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>D</sub>** after 180 min of sonication in THF (15 mL) and  $\text{D}_2\text{O}$  (0.2 mL).



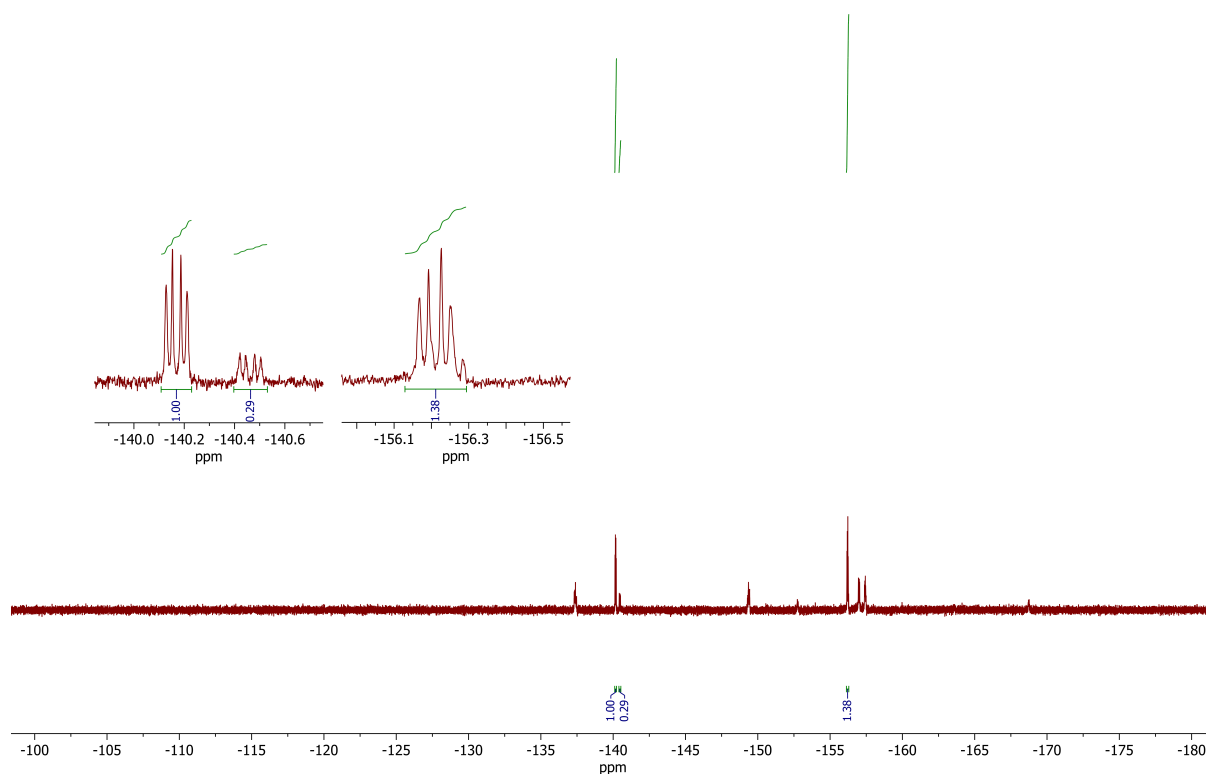


**Spectrum 99.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL). 100% of the formed tetrafluorobenzene species is protonated.

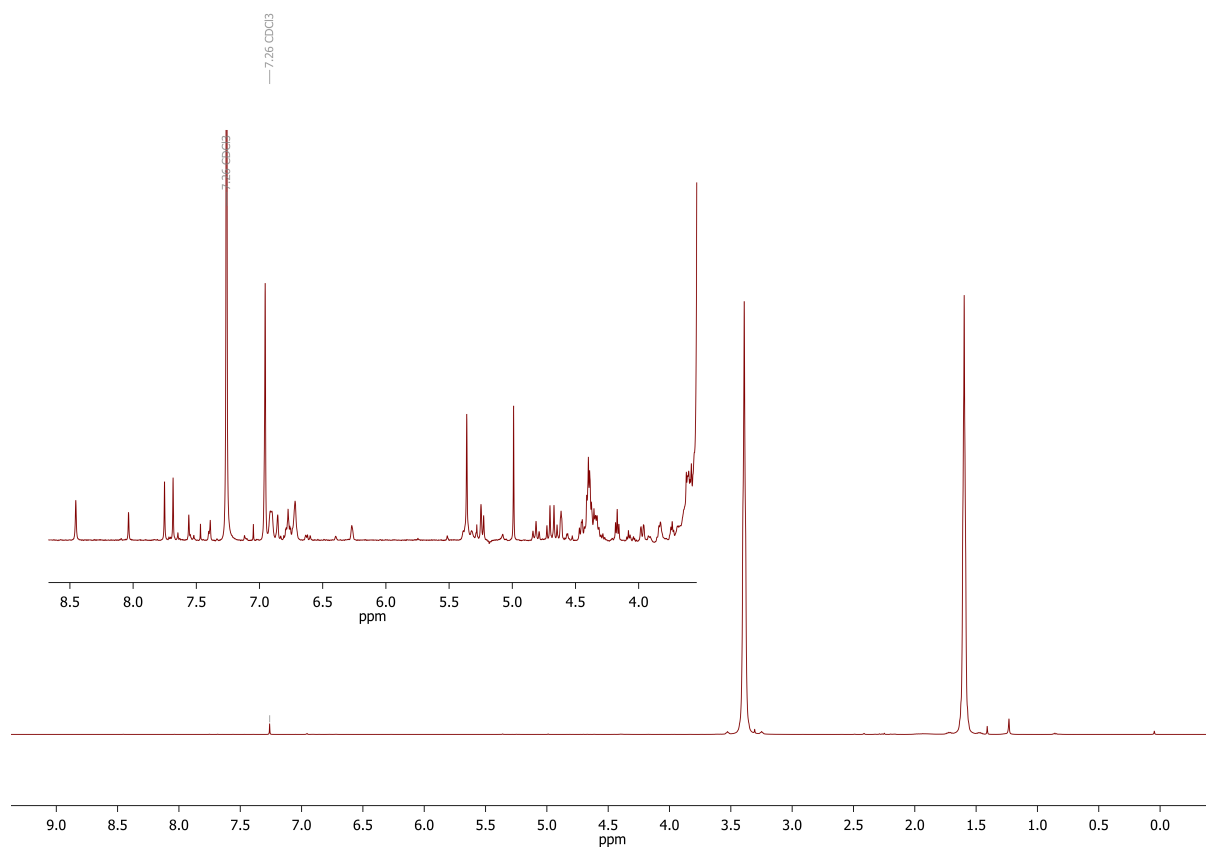


**Spectrum 100.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1<sub>D</sub>** after 180 min of sonication in THF (15 mL).

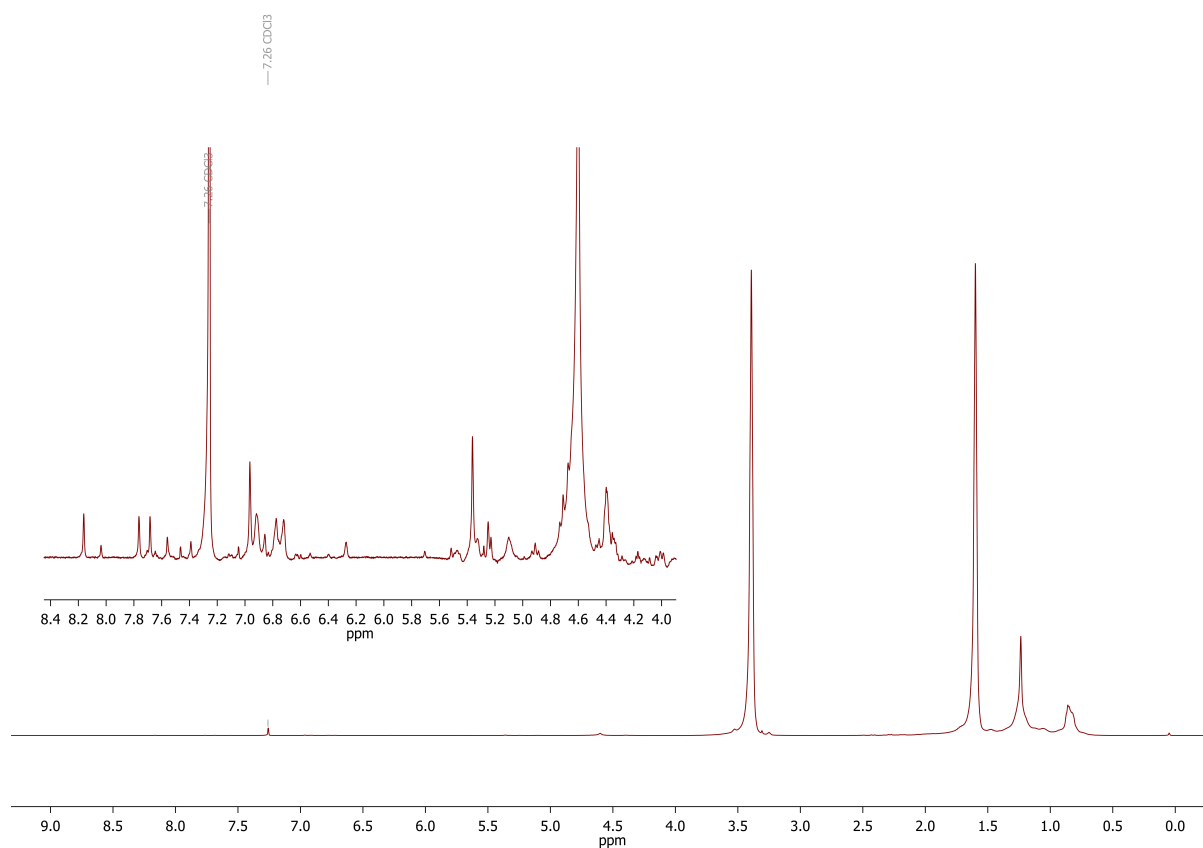




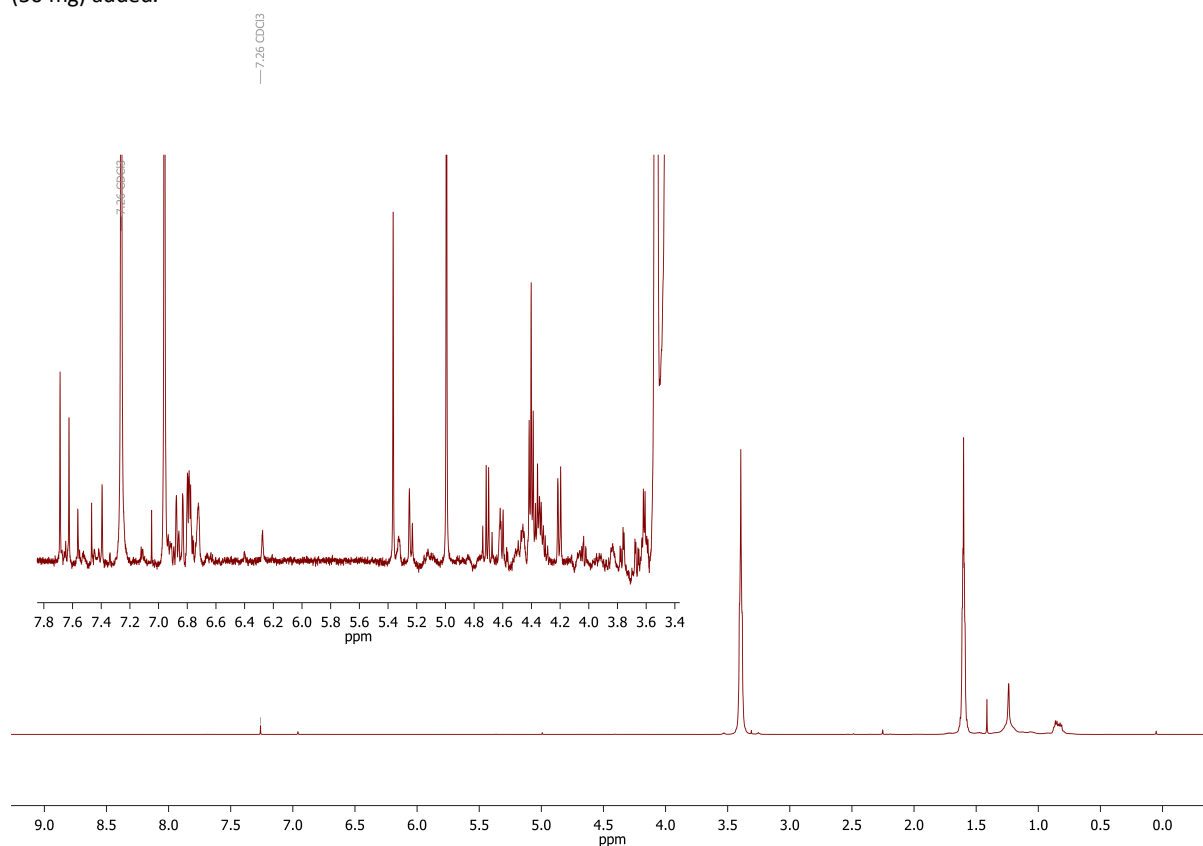
**Spectrum 101.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **1D** after 180 min of sonication in THF (15 mL). Approximately 22% of the formed tetrafluorobenzene species is deuterated.



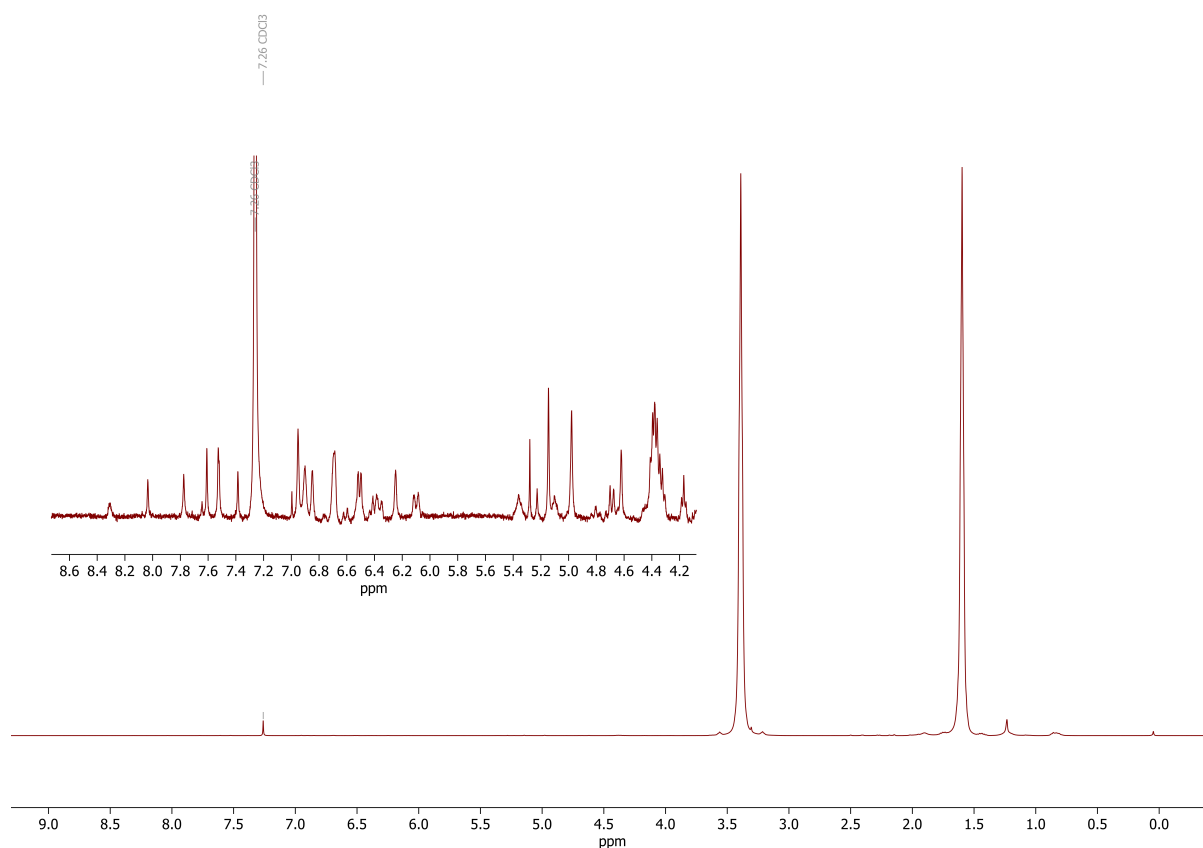
**Spectrum 102.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **1H** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL) with  $\text{NH}_4\text{Cl}$  (50 mg) added.



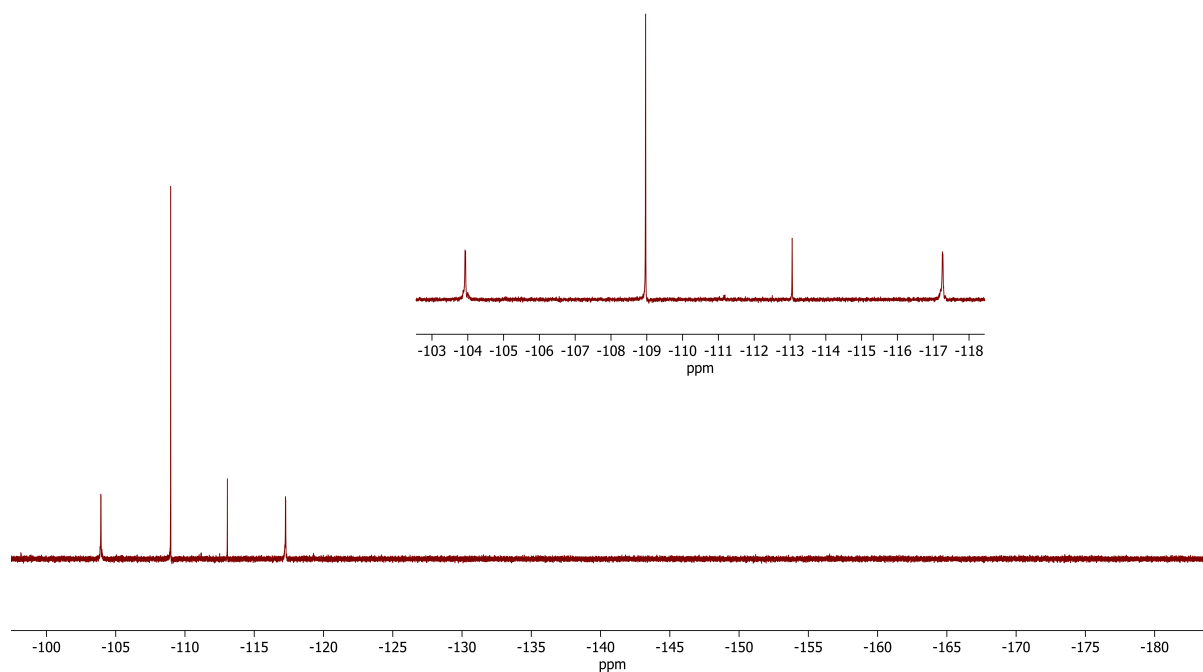
**Spectrum 103.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL) with LiBr (50 mg) added.



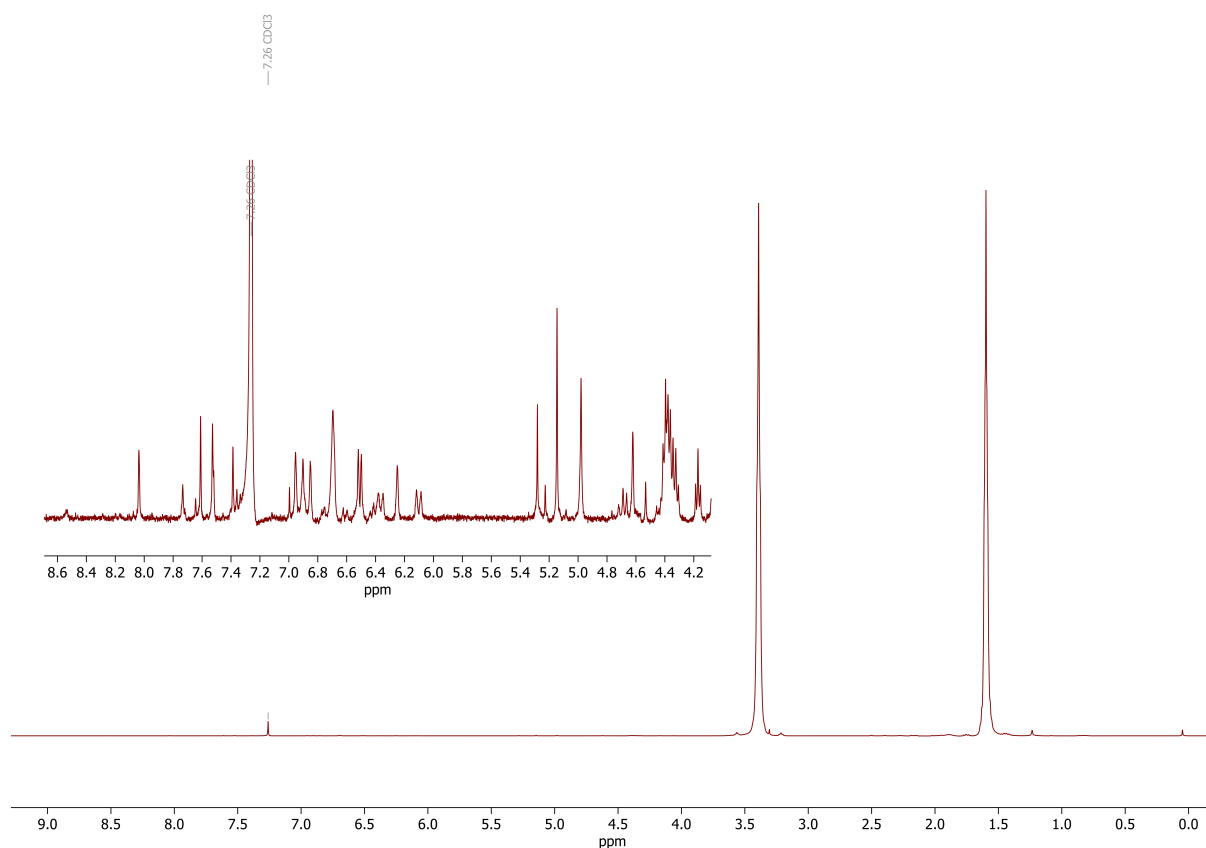
**Spectrum 104.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **1<sub>H</sub>** after 180 min of sonication in THF (15 mL) and H<sub>2</sub>O (0.2 mL) with NH<sub>4</sub>Cl (50 mg) added followed by deprotonation using NaH (60% in mineral oil, 5 mg) and reaction with CS<sub>2</sub> (0.2 mL) in dry THF (5 mL).



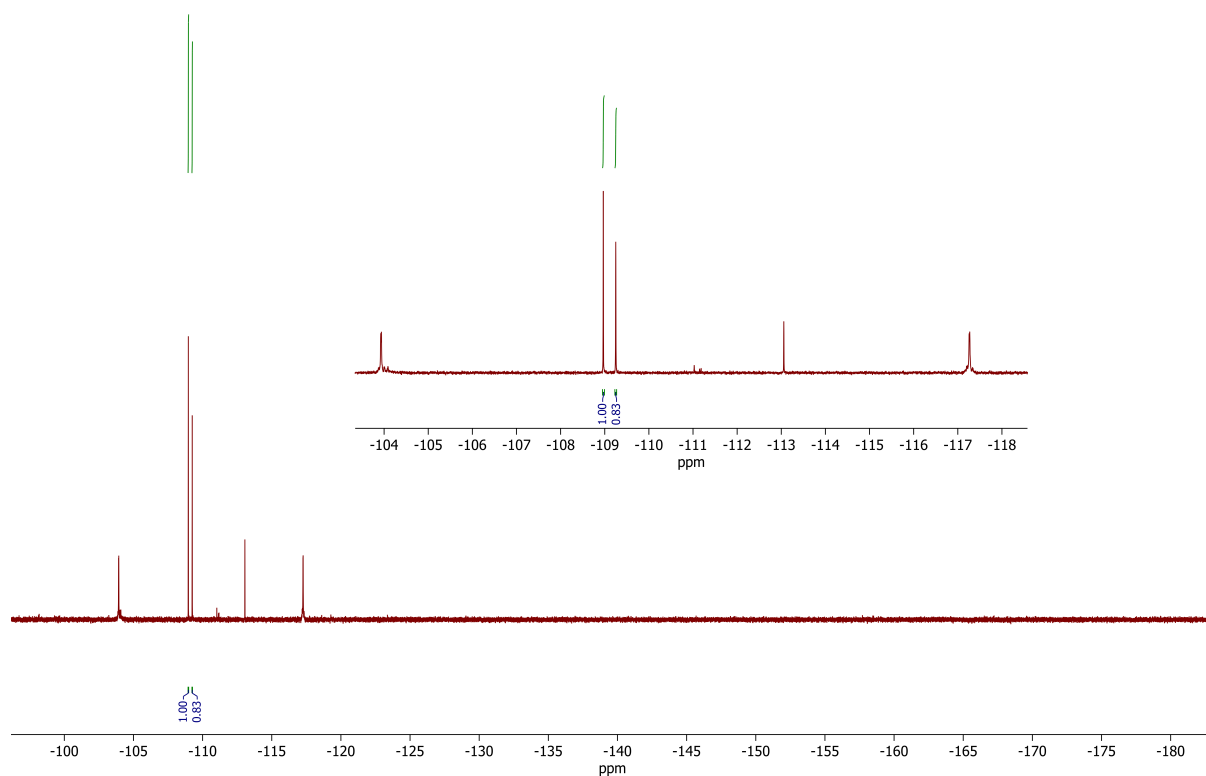
**Spectrum 105.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **8a** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL).



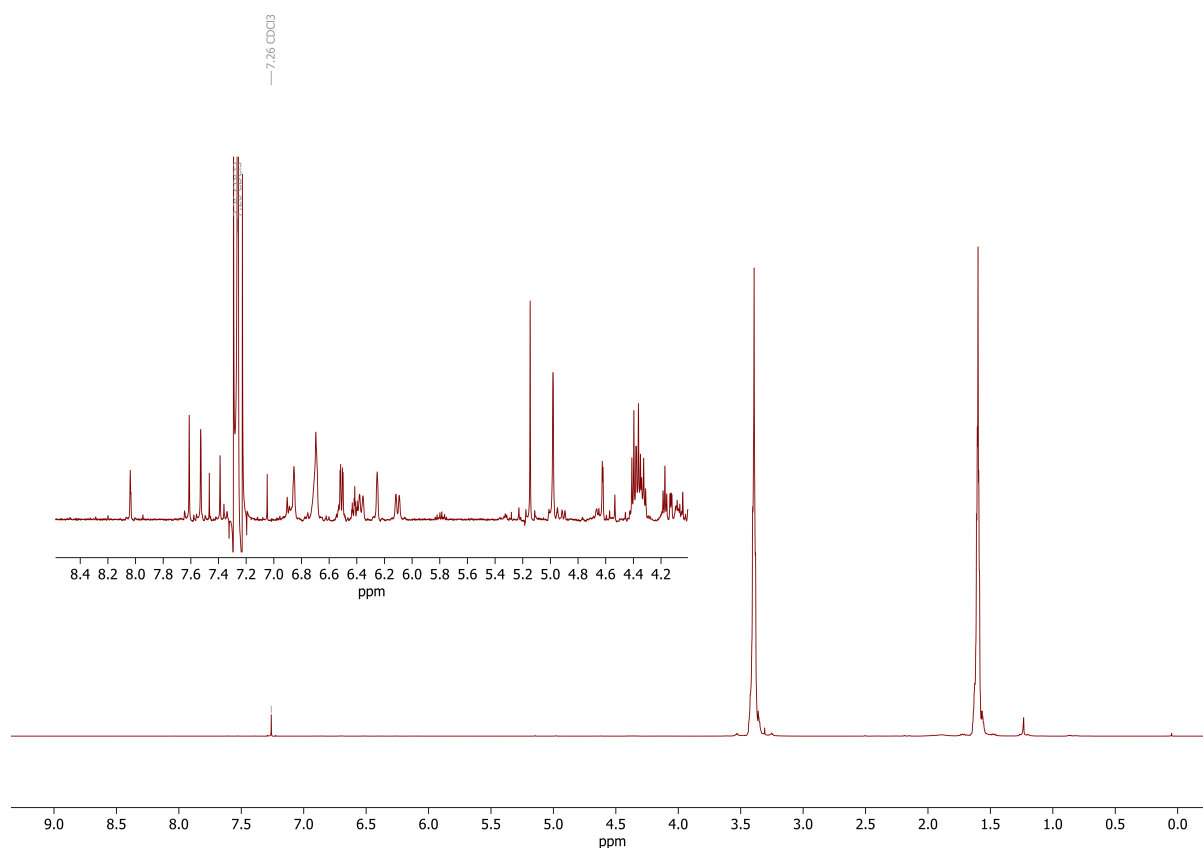
**Spectrum 106.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **8a** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL). 100% of the formed difluorobenzene species is protonated.



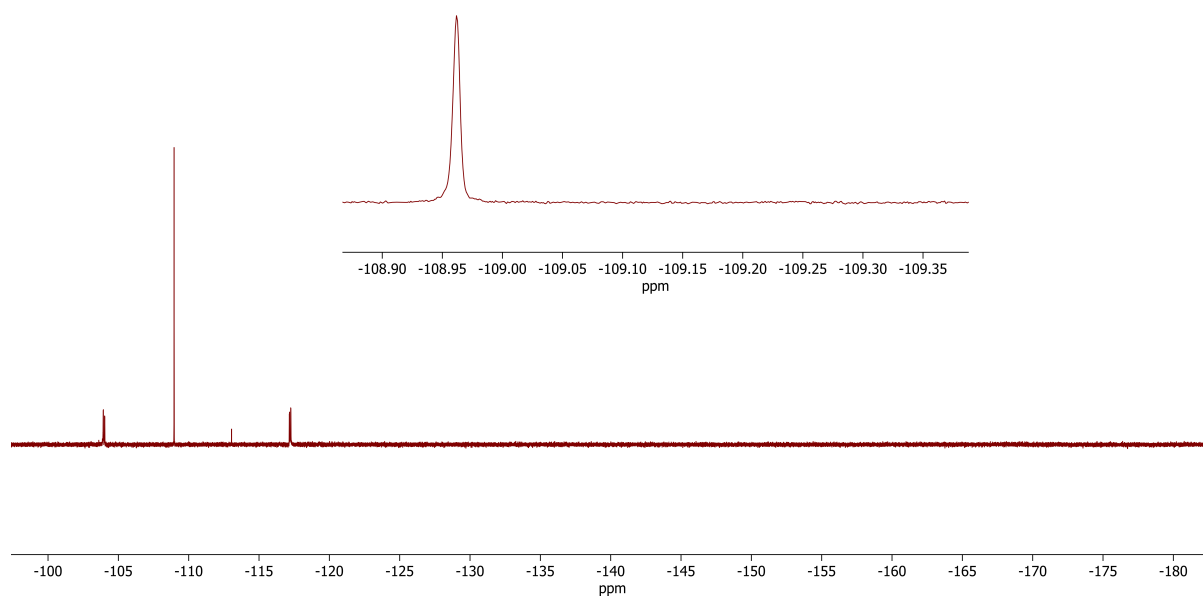
**Spectrum 107.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **8a** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL).



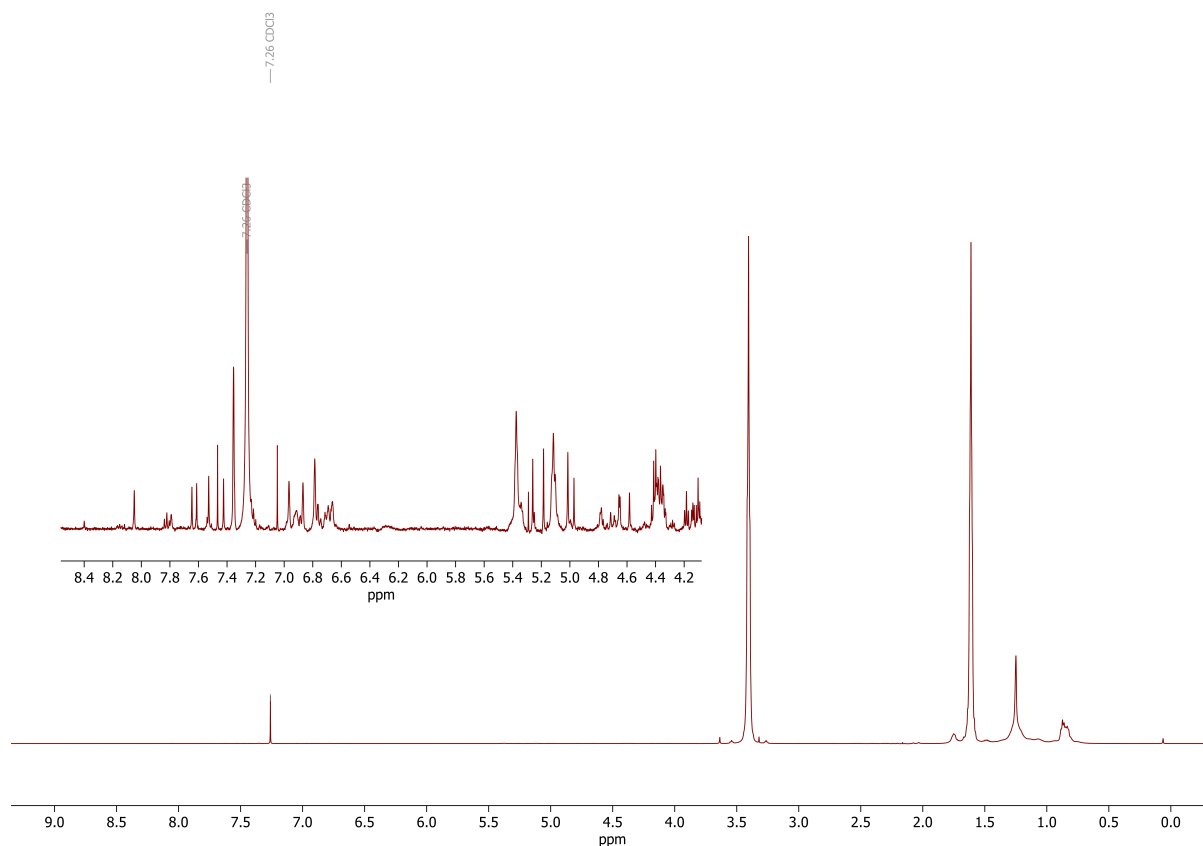
**Spectrum 108.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **8a** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL). Approximately 45% of the formed difluorobenzene species is deuterated.



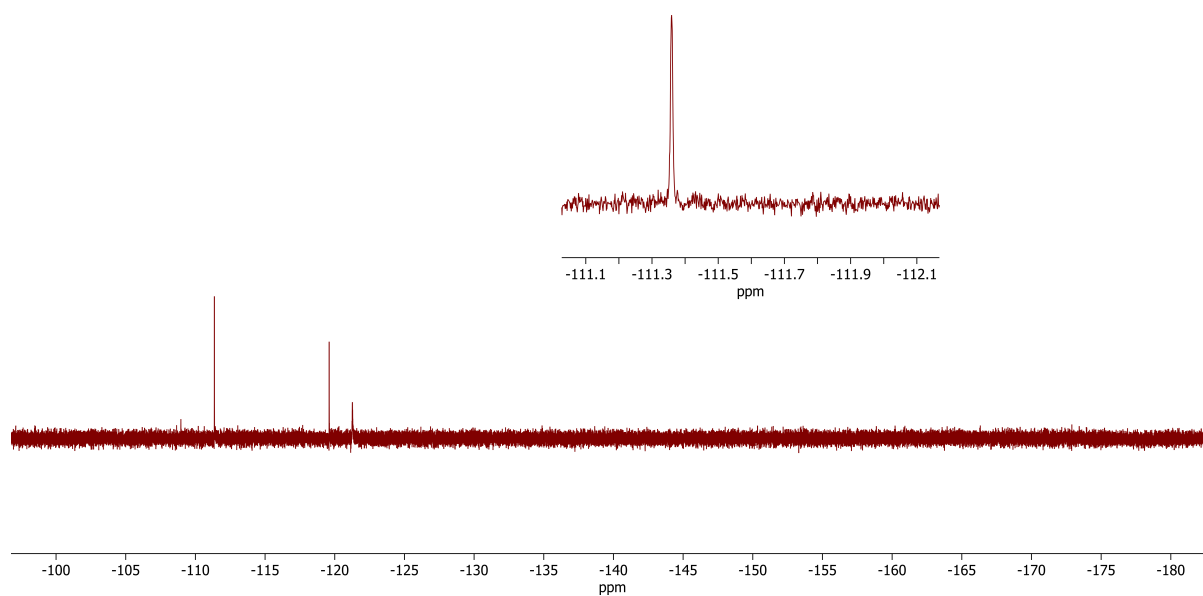
**Spectrum 109.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **8a** after 180 min of sonication in THF-d<sub>8</sub> (1 mL), benzene (14 mL) and H<sub>2</sub>O (0.2 mL).



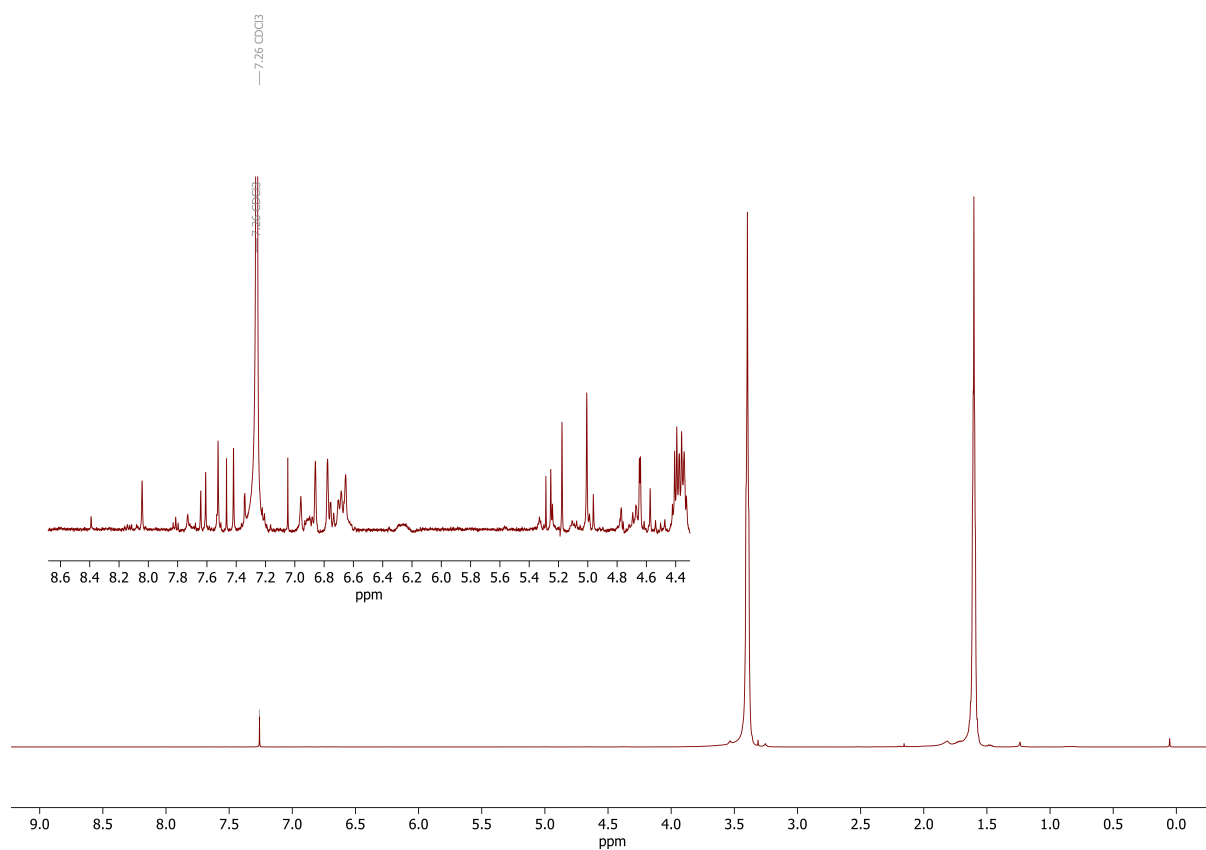
**Spectrum 110.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **8a** after 180 min of sonication in THF-d<sub>8</sub> (1 mL), benzene (14 mL) and H<sub>2</sub>O (0.2 mL). None of the formed difluorobenzene species can be observed as being deuterated.



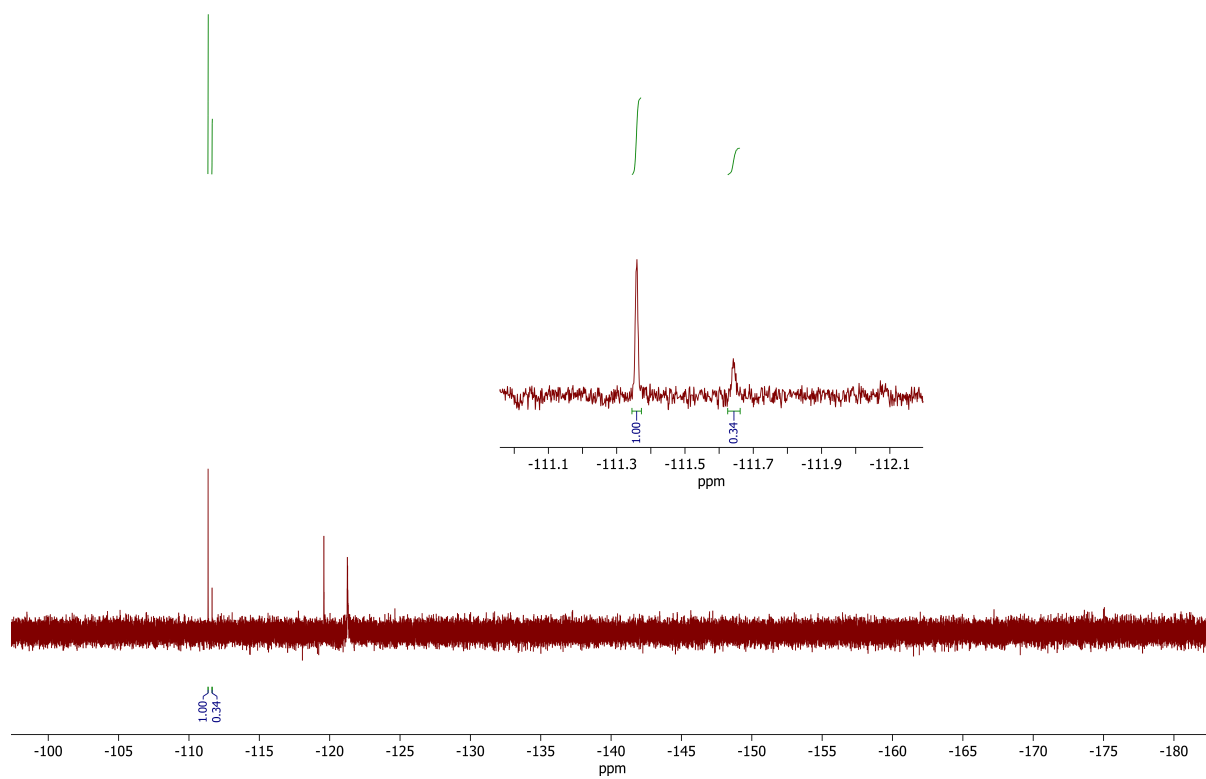
**Spectrum 111.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **8b** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL).



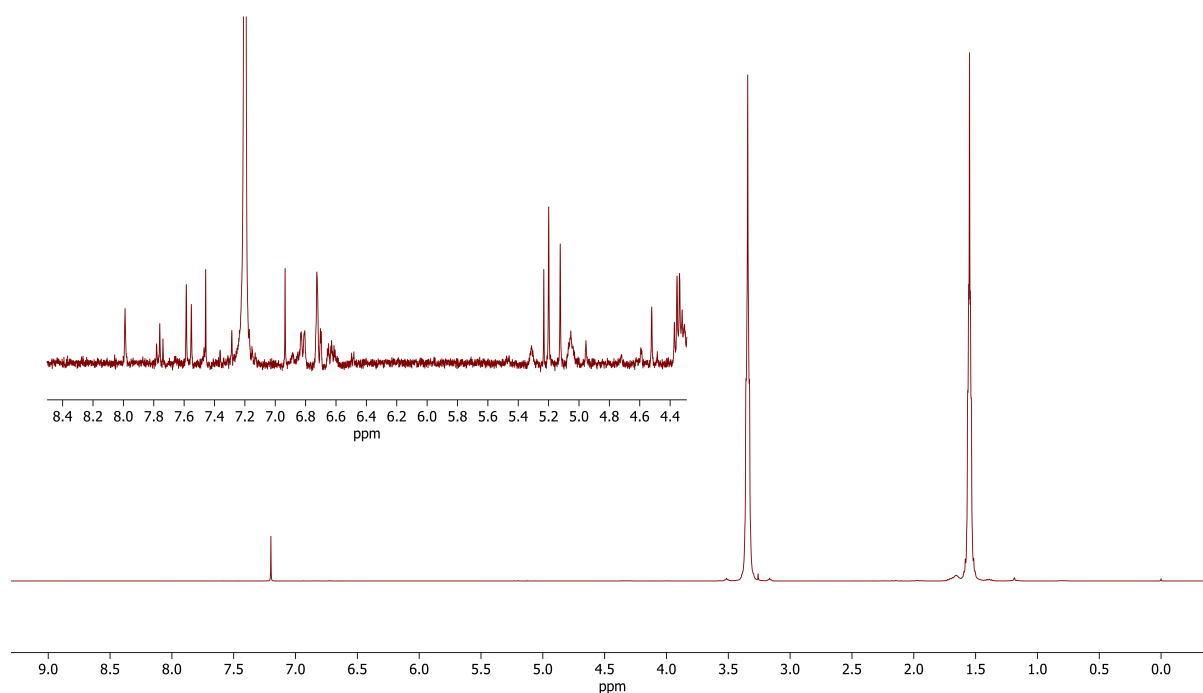
**Spectrum 112.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **8b** after 180 min of sonication in THF (15 mL) and  $\text{H}_2\text{O}$  (0.2 mL). 100% of the formed fluorobenzene species is protonated.



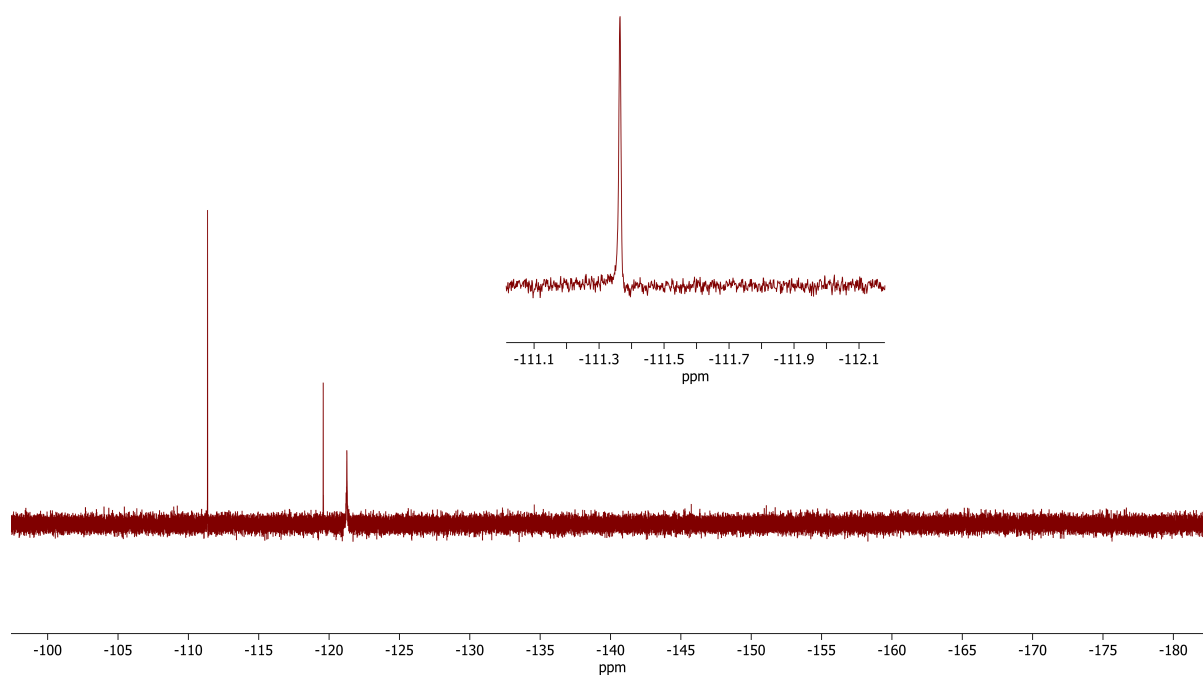
**Spectrum 113.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) of **8b** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL).



**Spectrum 114.** <sup>19</sup>F NMR (376 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of **8b** after 180 min of sonication in THF (15 mL) and D<sub>2</sub>O (0.2 mL). Approximately 25% of the formed fluorobenzene species is deuterated.



**Spectrum 115.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 298 K) of **8b** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL).

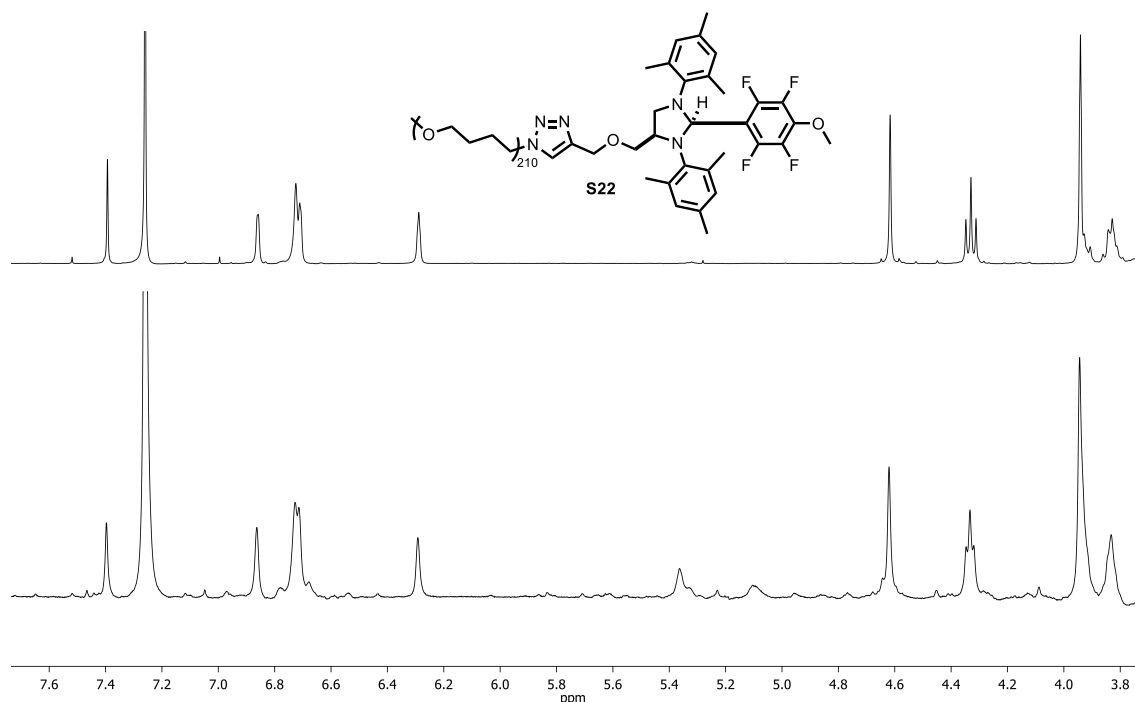


**Spectrum 116.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) of **8b** after 180 min of sonication in THF- $\text{d}_8$  (1 mL), benzene (14 mL) and  $\text{H}_2\text{O}$  (0.2 mL). None of the formed fluorobenzene species can be observed as being deuterated.

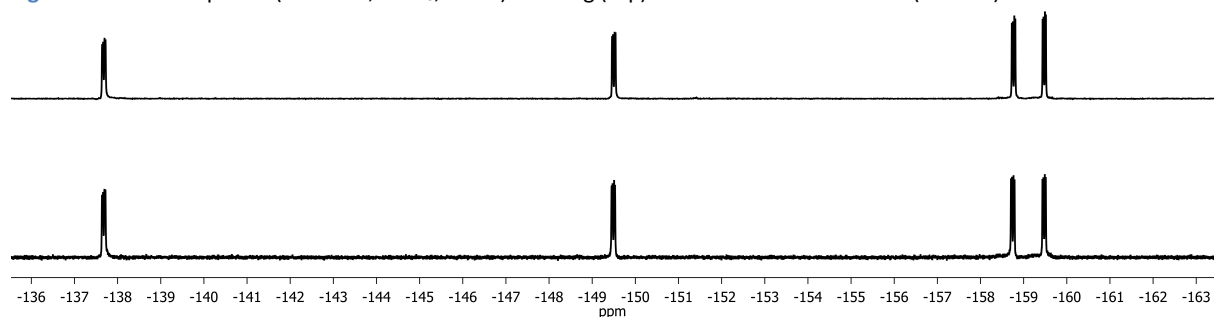


## 9 Control Experiment

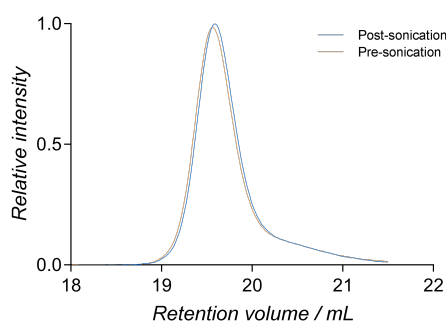
In order to prove that cleavage of the mechanophores was due to mechanical activation, and not other effects such as thermal activation, we subjected **S22**, a derivative of **1<sub>H</sub>** positioned terminally in a chain of PTHF, to the same sonication experiments used to cleave **1<sub>H</sub>** and **1<sub>D</sub>**, as described in Section 8. Analysis of the polymer post-sonication by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy (Figures 16 and 17) showed no change in signals and hence no cleavage of the mechanophore while GPC traces (Figure 18) additionally showed no cleavage of the polymer chain.



**Figure 16.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CDCl}_3$ , 298 K) showing (top) **S22** before sonication and (bottom) **S22** after sonication.



**Figure 17.**  $^{19}\text{F}$  NMR spectra (376 MHz,  $\text{C}_6\text{D}_6$ , 298 K) showing (top) **S22** before sonication and (bottom) **S22** after sonication.

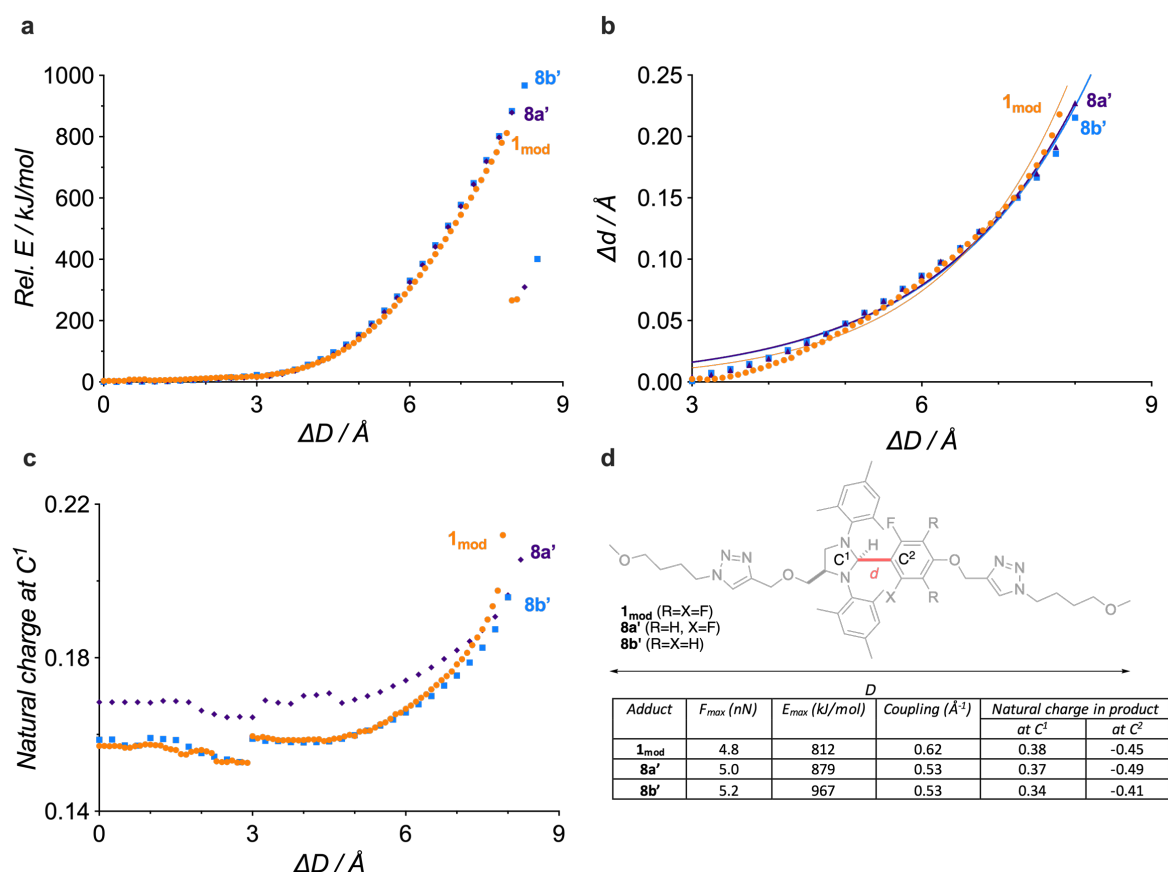


**Figure 18.** GPC traces of **S22** before and after sonication.

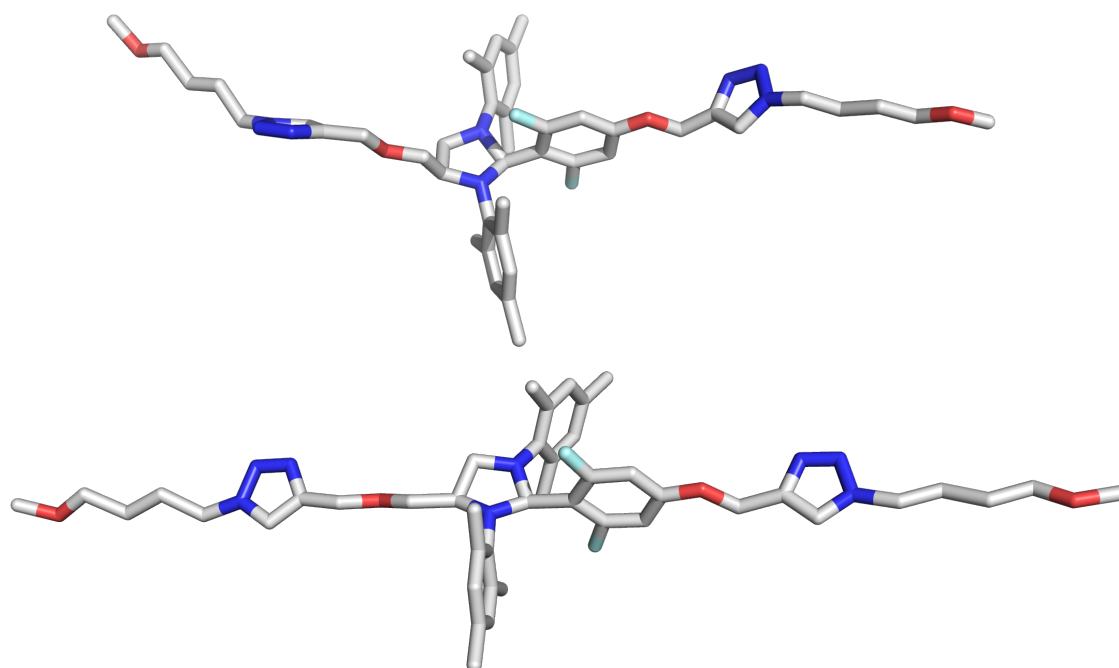
## 10 Calculations

### 10.1 CoGEF

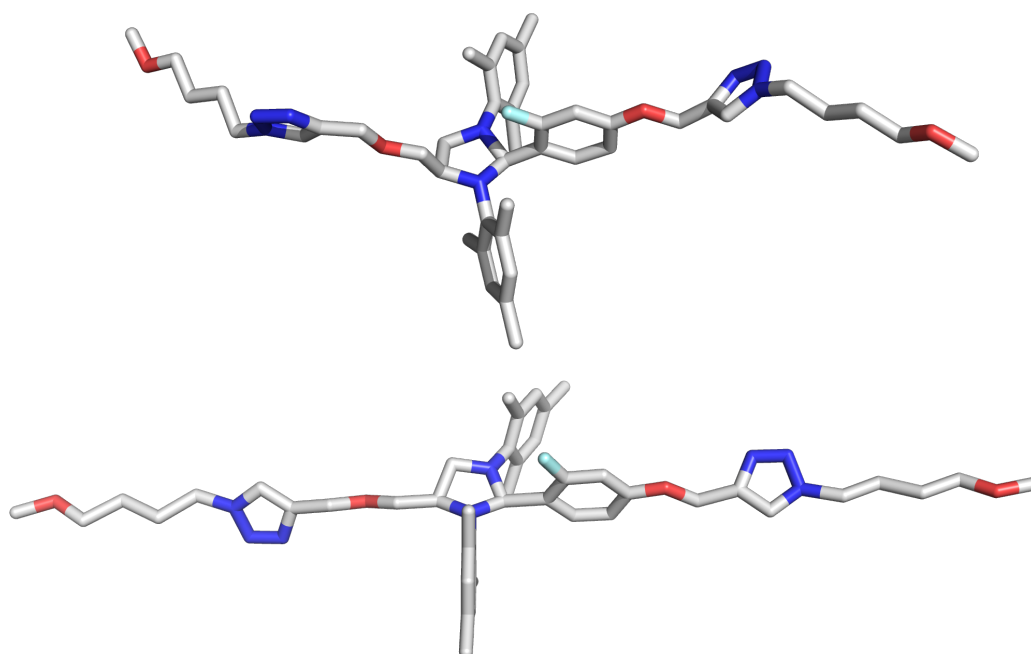
CoGEF calculations were performed on Spartan '14 following Beyer's method<sup>2</sup>. The structure of the mechanophore was built in Spartan '14 and minimized using molecular mechanics (MMFF). The distance between the terminal methyl groups was constrained and increased by increments of 0.1 Å (**1<sub>mod</sub>**) or 0.25 Å (**8a-b'**). At each step, the energy was minimized by molecular mechanics (MMFF) then DFT (B3LYP/6-31G\*) in vacuum. The relative energy of each intermediate was determined by setting the energy of the initial state at 0 kJ/mol.  $F_{\max}$  values were determined from the slope of the final 40% of the energy/elongation curve (i.e. from 0.6  $E_{\max}$  to  $E_{\max}$ ).



**Figure 19.** Evolution of energy (a), scissile bond length (b), and natural charge at C<sup>1</sup> (c) of model mechanophores (d) upon simulated elongation (CoGEF, DFT B3LYP/6-31G\*). (c) activation parameters.  $F_{\max}$  determined from the slope of the final 40% of the energy/elongation curve. The mechanochemical coupling is defined as the slope of the exponential fit ( $R^2 = 0.982, 0.988, 0.989$  for **1<sub>mod</sub>**, **8a'**, and **8b'** respectively) in (b). Second and third order polynomial models didn't improve the fit.

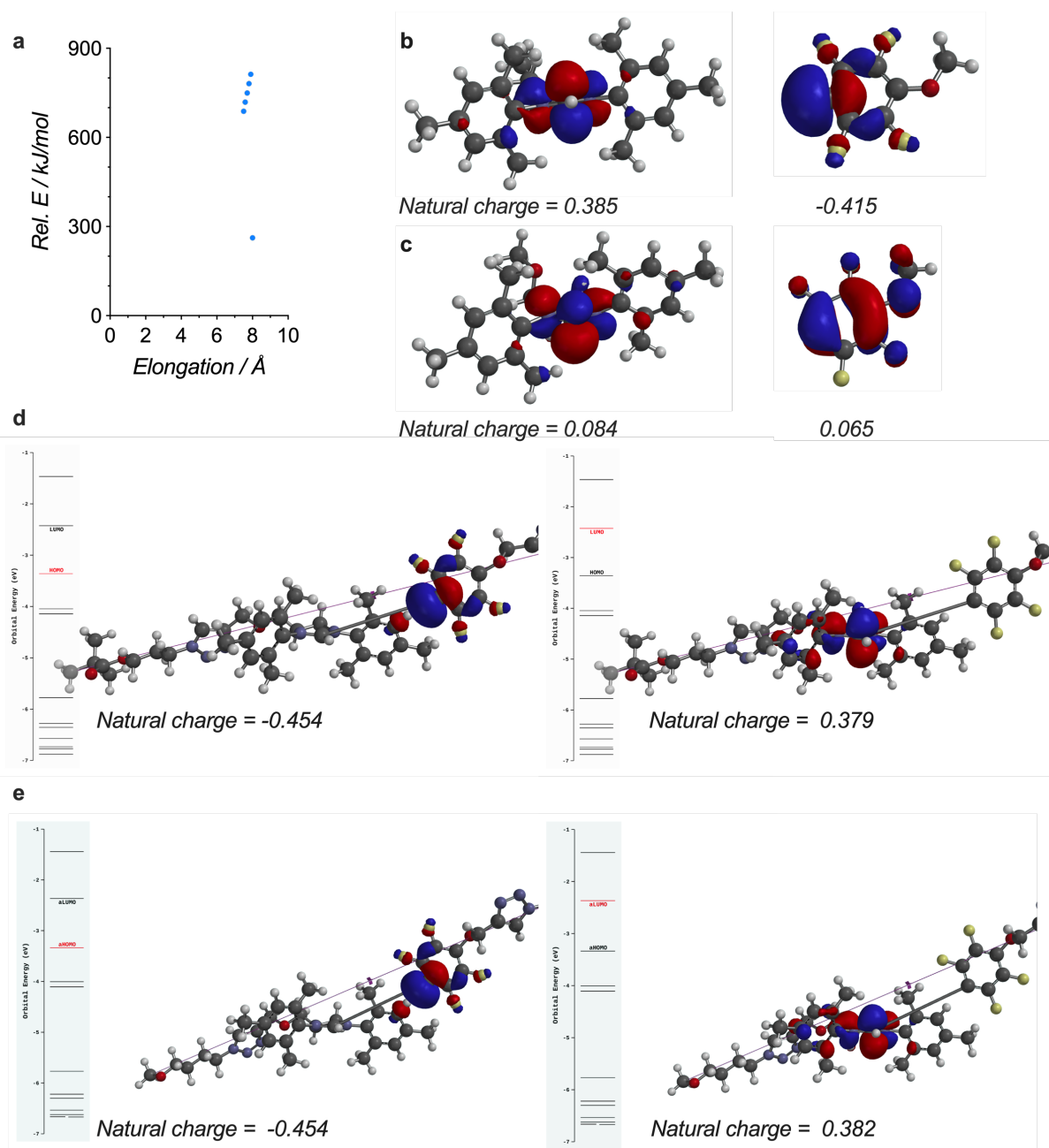


**Figure 20.** CoGEF structures of mechanophore **8a'** at  $E_0$  (top) and  $E_{\max}$  (bottom). Hydrogen atoms are omitted for clarity.



**Figure 21.** CoGEF structures of mechanophore **8b'** at  $E_0$  (top) and  $E_{\max}$  (bottom). Hydrogen atoms are omitted for clarity.

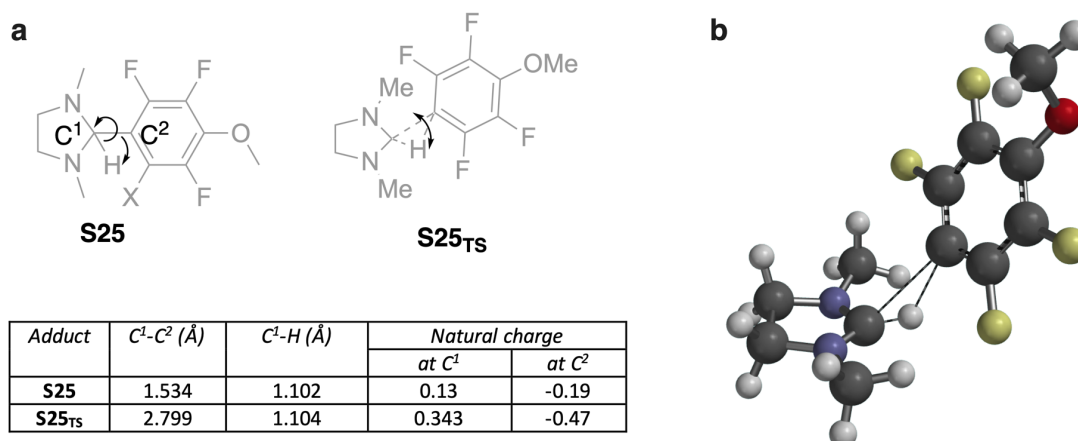
The heterolytic nature of the cleavage observed in the CoGEF experiments was confirmed by recalculating the terminal portion (Fig.S22a) of the **1<sub>mod</sub>** CoGEF profile by unrestricted DFT (UB3LYP/6-31G\*). Orbital shapes and natural charges are consistent with a heterolytic process (Fig.22b-e).



**Figure 22.** The partial CoGEF curve (a) of  $\mathbf{1}_{\text{mod}}$  computed with unrestricted DFT (UB3LYP/6-31G\*) shows a profile similar to Fig.19a. LUMO (b, left) and HOMO (b, right) orbitals of model imidazolium and tetrafluoroarene respectively computed by DFT (B3LYP/6-31G\*). SOMO orbitals of model imidazolidine (c, left) and tetrafluoroarene (c, right) respectively computed by unrestricted DFT (UB3LYP/6-31G\*). HOMO (left) and LUMO (right) orbitals of cleaved  $\mathbf{1}_{\text{mod}}$  structure from restricted (d) and unrestricted (e) CoGEF calculations.

## 10.2 Transition-state

Model **S25** was used to calculate the geometry of the TS of the concerted elimination of the tetrafluoroarene derivative. A preliminary structure was found using the TS search algorithm implemented in Spartan '14 (i.e. built around a TS present in Spartan '14 database, in this case a TS calculated for the insertion of methylene carbene into a methane C-H bond) and its geometry was optimised by DFT (B3LYP/6-31G\*, vacuum). The computed structure presents a single imaginary vibration corresponding to a rocking movement that aligns the C<sup>1</sup>-H bond with C<sup>1</sup>-C<sup>2</sup> during the planarization of the C<sup>1</sup> centre.



**Figure 23.** Structures (a) of model mechanophore **S23** (arrows indicate the electronic movements used in the search algorithm) and TS **S25<sub>TS</sub>** (double arrow indicates the rocking movement of the imaginary frequency). (b) Calculated geometry for **S25<sub>TS</sub>**.

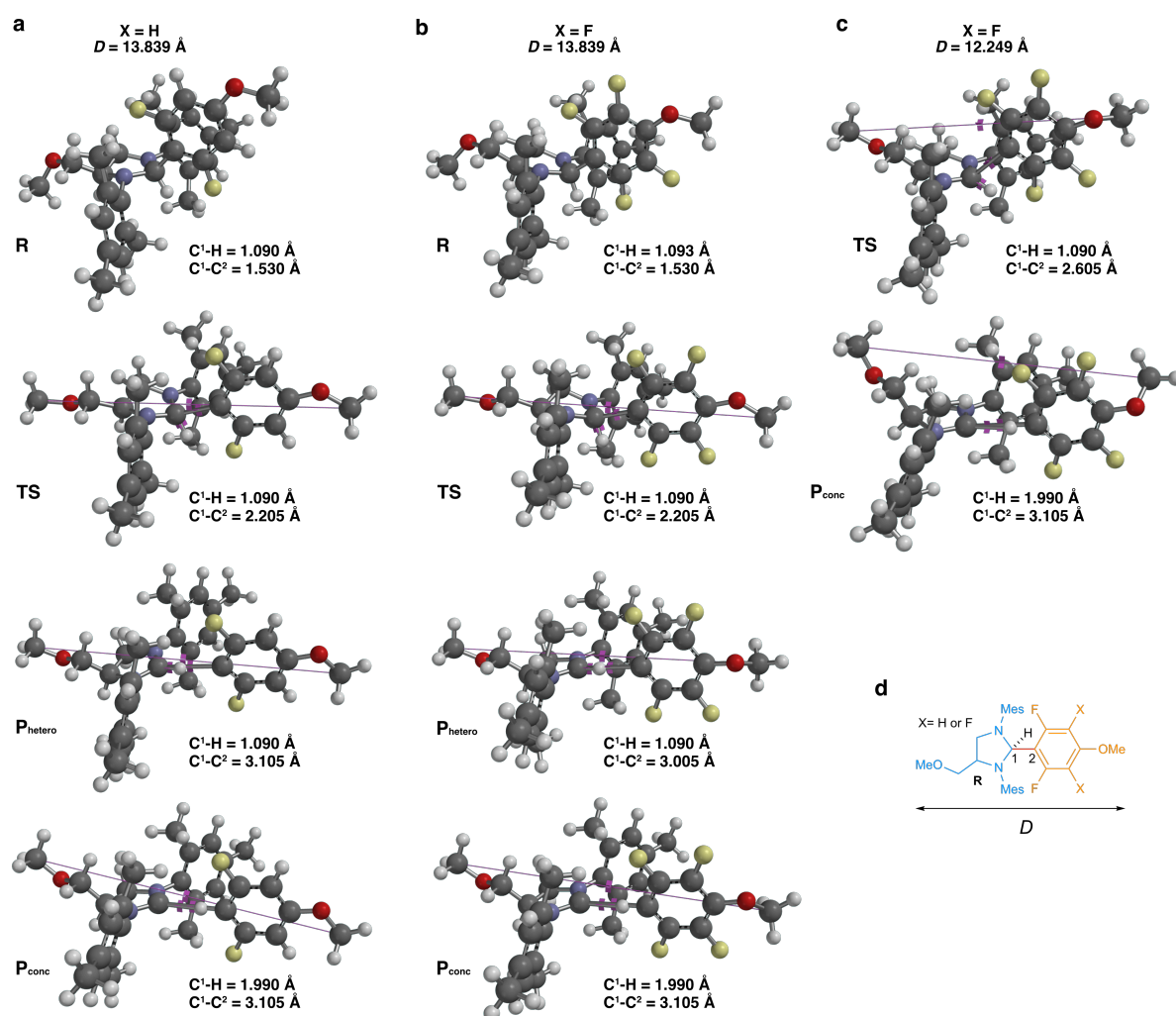
**Table 5.** Calculated coordinates and IR values for **S25** and **S25<sub>TS</sub>**

| S25 coordinate |           |           |           | S25 <sub>TS</sub> coordinate |           |           |           | S25 <sub>TS</sub> IR          |           |                               |           |
|----------------|-----------|-----------|-----------|------------------------------|-----------|-----------|-----------|-------------------------------|-----------|-------------------------------|-----------|
|                |           |           |           |                              |           |           |           | Frequency (cm <sup>-1</sup> ) | Intensity | Frequency (cm <sup>-1</sup> ) | Intensity |
| N              | 3.392529  | -0.848680 | -0.477390 | N                            | 3.392529  | -0.848680 | -0.477390 | -176                          | 91.70     | 637                           | 0.15      |
| C              | 2.747010  | 0.316870  | -0.498295 | C                            | 2.747010  | 0.316870  | -0.498295 | 22                            | 2.61      | 651                           | 30.00     |
| N              | 3.107488  | 1.108592  | 0.503223  | N                            | 3.107488  | 1.108592  | 0.503223  | 28                            | 1.86      | 673                           | 1.43      |
| C              | 4.125691  | 0.458426  | 1.342010  | C                            | 4.125691  | 0.458426  | 1.342010  | 42                            | 3.31      | 715                           | 1.20      |
| C              | 4.129583  | -0.987441 | 0.791536  | C                            | 4.129583  | -0.987441 | 0.791536  | 62                            | 3.51      | 730                           | 6.57      |
| H              | 1.849049  | 0.486766  | -1.117382 | H                            | 1.849049  | 0.486766  | -1.117382 | 84                            | 0.73      | 849                           | 3.02      |
| H              | 5.094855  | 0.958478  | 1.217047  | H                            | 5.094855  | 0.958478  | 1.217047  | 111                           | 0.60      | 920                           | 11.24     |
| H              | 3.593007  | -1.680378 | 1.453529  | H                            | 3.593007  | -1.680378 | 1.453529  | 118                           | 9.29      | 929                           | 198.74    |
| H              | 5.136226  | -1.377552 | 0.618374  | H                            | 5.136226  | -1.377552 | 0.618374  | 120                           | 2.48      | 966                           | 1.11      |
| C              | -0.030428 | -0.008736 | -0.620319 | C                            | -0.030428 | -0.008736 | -0.620319 | 133                           | 11.42     | 973                           | 68.96     |
| C              | -2.845150 | -0.015388 | -0.092871 | C                            | -2.845150 | -0.015388 | -0.092871 | 147                           | 26.48     | 987                           | 6.53      |
| C              | -0.809279 | 1.124445  | -0.686556 | C                            | -0.809279 | 1.124445  | -0.686556 | 167                           | 1.14      | 1083                          | 6.08      |
| C              | -0.718438 | -1.150428 | -0.268961 | C                            | -0.718438 | -1.150428 | -0.268961 | 189                           | 17.52     | 1100                          | 235.98    |
| C              | -2.087232 | -1.191219 | -0.018423 | C                            | -2.087232 | -1.191219 | -0.018423 | 195                           | 14.79     | 1111                          | 2.13      |
| C              | -2.177537 | 1.167855  | -0.429966 | C                            | -2.177537 | 1.167855  | -0.429966 | 207                           | 4.87      | 1116                          | 104.05    |
| O              | -4.203021 | 0.000390  | 0.107288  | O                            | -4.203021 | 0.000390  | 0.107288  | 242                           | 7.43      | 1128                          | 40.37     |
| C              | -4.613111 | -0.274367 | 1.447401  | C                            | -4.613111 | -0.274367 | 1.447401  | 251                           | 15.04     | 1165                          | 25.67     |
| H              | -5.701266 | -0.173859 | 1.458398  | H                            | -5.701266 | -0.173859 | 1.458398  | 275                           | 1.46      | 1181                          | 12.18     |
| H              | -4.174644 | 0.447806  | 2.149448  | H                            | -4.174644 | 0.447806  | 2.149448  | 285                           | 6.09      | 1183                          | 3.70      |
| H              | -4.336568 | -1.290194 | 1.749588  | H                            | -4.336568 | -1.290194 | 1.749588  | 290                           | 14.26     | 1204                          | 35.96     |
| F              | -0.055189 | -2.358216 | -0.142668 | F                            | -0.055189 | -2.358216 | -0.142668 | 302                           | 167.52    | 1222                          | 2.49      |
| F              | -2.708117 | -2.351015 | 0.316654  | F                            | -2.708117 | -2.351015 | 0.316654  | 318                           | 41.61     | 1231                          | 49.92     |
| F              | -2.873214 | 2.324352  | -0.495412 | F                            | -2.873214 | 2.324352  | -0.495412 | 337                           | 12.09     | 1256                          | 11.25     |
| F              | -0.216856 | 2.339971  | -1.004538 | F                            | -0.216856 | 2.339971  | -1.004538 | 399                           | 35.84     | 1260                          | 3.78      |
| H              | 3.843845  | 0.509465  | 2.398696  | H                            | 3.843845  | 0.509465  | 2.398696  | 406                           | 0.87      | 1306                          | 154.35    |
| C              | 2.947491  | -2.015811 | -1.229191 | C                            | 2.947491  | -2.015811 | -1.229191 | 425                           | 0.06      | 1318                          | 20.53     |
| H              | 2.522715  | -1.684878 | -2.177525 | H                            | 2.522715  | -1.684878 | -2.177525 | 447                           | 0.74      | 1340                          | 46.84     |
| H              | 2.169219  | -2.553347 | -0.678319 | H                            | 2.169219  | -2.553347 | -0.678319 | 470                           | 4.01      | 1353                          | 62.96     |
| H              | 3.804314  | -2.665021 | -1.428004 | H                            | 3.804314  | -2.665021 | -1.428004 | 555                           | 6.86      | 1354                          | 8.87      |
| C              | 2.600364  | 2.449728  | 0.737206  | C                            | 2.600364  | 2.449728  | 0.737206  | 587                           | 2.12      | 1386                          | 4.81      |
| H              | 3.365687  | 3.203731  | 0.515231  | H                            | 3.365687  | 3.203731  | 0.515231  | 604                           | 2.26      | 1447                          | 404.65    |
| H              | 2.301564  | 2.547477  | 1.786589  | H                            | 2.301564  | 2.547477  | 1.786589  | 620                           | 7.08      | 1477                          | 123.00    |
| H              | 1.722654  | 2.609569  | 0.107432  | H                            | 1.722654  | 2.609569  | 0.107432  |                               |           |                               |           |

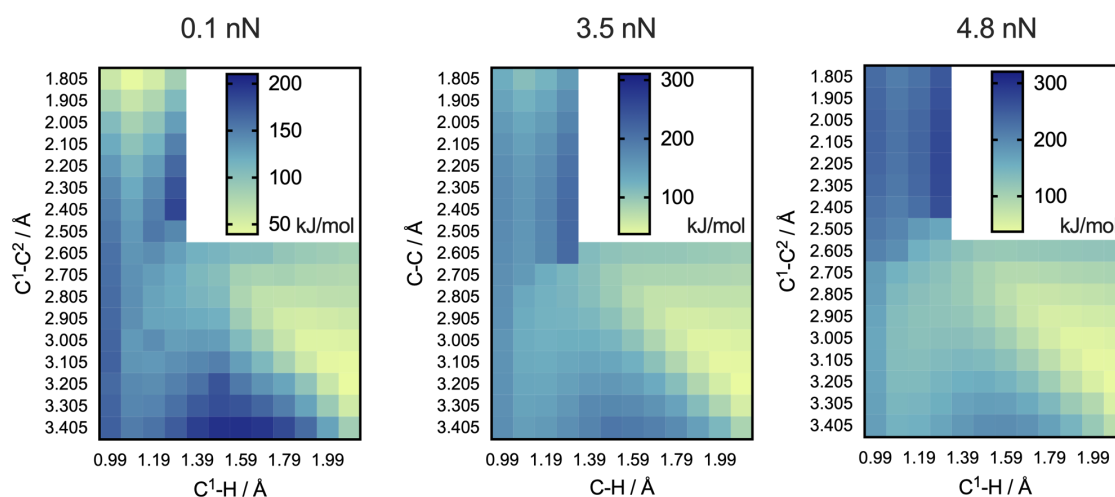
Energy : -1049.707024 hartrees      Energy : -1049.646002 hartrees

### 10.3 Force-modified potential energy surfaces

PES calculations were performed on Spartan '14. The structure of the model mechanophore **R** was built in Spartan '14 and minimized using molecular mechanics (MMFF). The distance between the terminal methyl groups was constrained ( $D = 12.249\text{\AA}$  (low-force) or  $13.839\text{\AA}$  ( $E_{max}$ )), and  $\text{C}^1\text{-C}^2$  and  $\text{C}^1\text{-H}$  bond lengths were increased by increments of  $0.1\text{\AA}$  from  $1.805\text{\AA}$  to  $3.405\text{\AA}$ , and  $0.99\text{\AA}$  to  $2.09\text{\AA}$  respectively. At each step, the energy was minimized by molecular mechanics (MMFF) then DFT (B3LYP/6-31G\*) in vacuum. The relative energy of each intermediate was determined by setting the energy of the force-free state at  $0\text{ kJ/mol}$ . The energy values associated with the heterolytic pathway are probably overestimated due to the lack of a solvent model.



**Figure 24.** Selected structures from the force-modified PES of bifluoro (a) and tetrafluoro (b, c) models (d).



**Figure 25.** PES (B3LYP/6-31G\*) for the dissociation of C<sup>1</sup>-C<sup>2</sup> (Fig. 24d, X=F) at 0.1 nN (left), 3.5 nN (middle), and 4.8 nN (right). The energy values associated with the heterolytic pathway are probably overestimated due to the lack of a solvent model.

## 11 References

1. Hickenboth, C. R. *et al.* Biasing reaction pathways with mechanical force. *Nature* **446**, 423–427 (2007).
2. Beyer, M. The mechanical strength of a covalent bond calculated by density functional theory. *J. Chem. Phys.* **112**, 7307–7312 (2000).